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Specification of Sulfur Forms in Coal

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SPECIATION OF SULFUR FORMS IN COAL

A Thesis

Presented to

the Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Weihao Wang

July 1994

SPECIATION OF SULFUR FORMS IN COAL

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Weihao Wang

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SPECIATION OF SULFUR FORMS IN COAL

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Over a century of studies of the organic chemistry of coal has led to many accomplishments in coal chemistry. The recognition of the role that sulfur plays in coal makes the speciation of sulfur in coal one of the most important research goals.

In this research solvent extraction, ultimate analysis, FTIR, TG-FTIR, sulfur methylation, and NMR techniques were employed to make quantitative and qualitative determinations of the organic sulfur in coal and its extracts.

The data obtained from those methods are discussed with regard to the analytical and synthetic approaches used. Carbon-sulfur bond cleavage at room temperature was observed during this research and was verified using reactions of model compounds.

Chapter I

INTRODUCTION

Coal is an aggregate of heterogeneous material composed mainly of organic and inorganic substances. The primary parts of the organic materials called macerals are vitrinite, exinite (or liptinite), and inertinite. Vitrinite is derived from woody tissues. Exinite is derived from spores, needles, leaf cuticles, and plant resins. Inertinite is derived from the partial carbonization of the coal-forming material by fire or intensive degradation by microorganisms. The inorganic substances contain primarily clay minerals such as aluminosilicates, quartz (mainly in the form of silica), carbonate minerals (principally as carbonates of Ca, Fe, Mg, and Mn), sulfides which are mostly pyrite and marcasite, sulfates usually found as variously hydrated iron sulfates ($\text{FeSO}_4 \cdot n\text{H}_2\text{O}$) and/or as jarosite (a mixed Na-K-Fe sulfate), and smaller amounts of other minerals.¹

Coal is thought to consist of a large matrix of clusters of fused aromatic rings connected by aliphatic bridges. The heterogeneous nature of coal precludes a detailed knowledge of its exact chemical structure. Several hypothetical chemical structures for coal macromolecules have been suggested,²⁻⁶ of which John H. Shinn possibly portrays the best model. Shinn's

model shows quantitatively the distribution of various bonds in coal, including wherever possible information concerning the details of bonding important to coal behavior (Figure 1).

Sulfur is present in coal in amounts varying from about 0.2 to over 10 percent by weight.⁷ The sulfur content in coal plays an important role in coal desulfurization and coal utilization, particularly in midwestern and eastern United States. Although the method of removing pyritic sulfur has been developed, the reduction of non-pyritic sulfur forms has been largely unsuccessful. The current analytical methods are not accurate in qualifying and quantifying the organic forms, a crucial step in understanding the chemistry affecting sulfur in coal.^{8,9}

A. Total Sulfur

Total sulfur data are necessary for the effective control of the emission of sulfuric oxides whenever coal is used as a fuel. During the burning of coal, sulfur is converted to oxides that may contribute to the corrosion of equipment, to the slagging of combustion or boiler equipment, and to atmospheric pollution. Total sulfur data are therefore necessary for evaluation of coals to be used for combustion purposes.

There are two ASTM methods for determining the total sulfur in coal and coke, with alternative procedures in each method. ASTM Method D 3177,¹⁰ "Total Sulfur in the Analysis

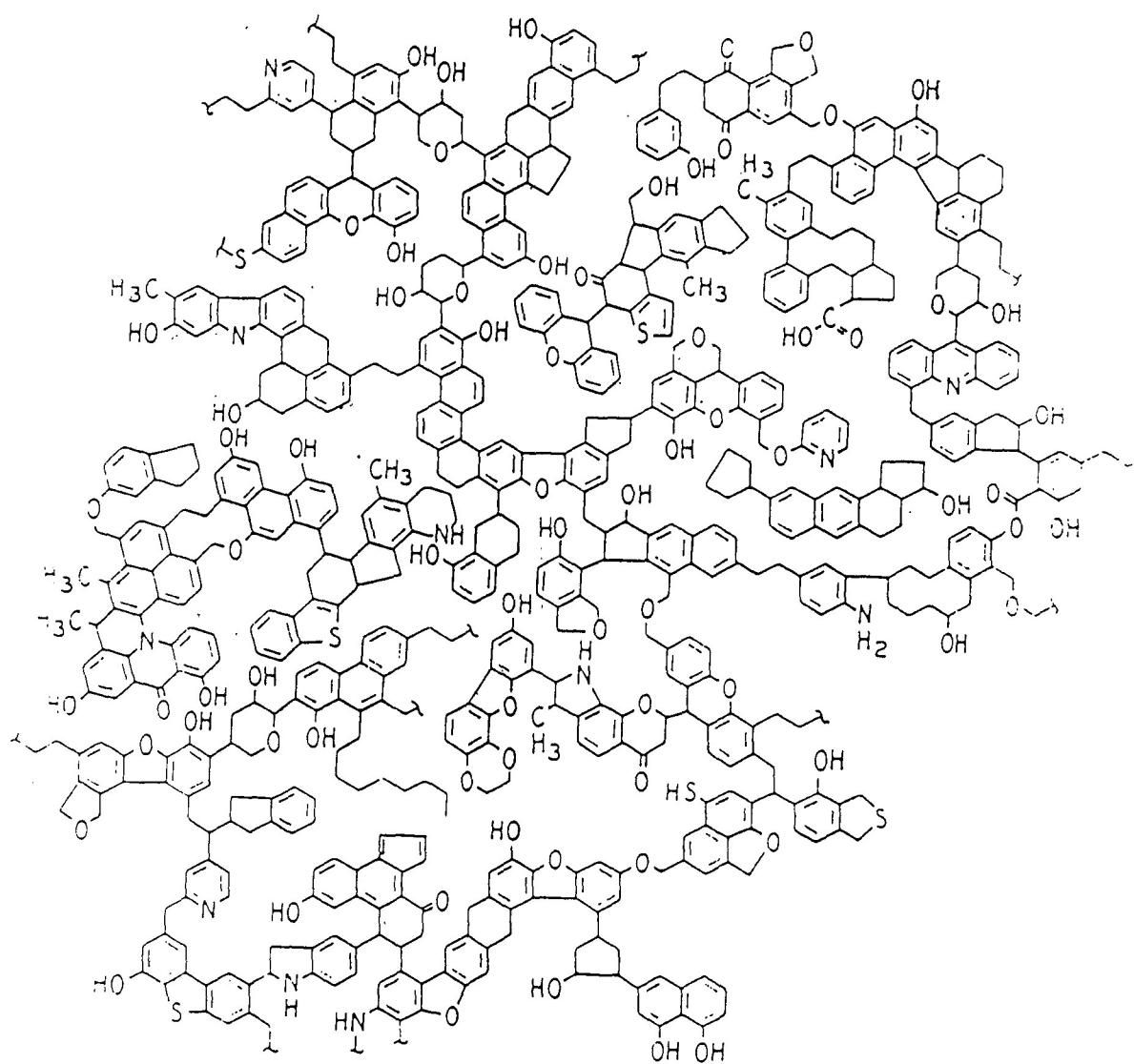


Figure 1. Model of bituminous coal structure.⁶

Sample of Coal and Coke," has two alternative procedures referred to as the Eschka and the bomb washing methods. ASTM Method D 4239,¹¹ "Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Method," has three alternative procedures. The basic difference in the three procedures is the method of detection of the sulfur dioxide produced in the combustion of the coal or coke sample. Method A uses an acid-base titration for detection, Method B uses a iodimetric titration, and Method C uses the absorption of infrared radiation for detection.

In ASTM Method C for sulfur determination the sulfur dioxide in the combustion gases is measured by the absorption of infrared (IR) radiation. Moisture and particulates are first removed from the gas stream by traps filled with anhydrous magnesium perchlorate. The gas stream is then passed through an IR absorption cell tuned to a frequency of radiation absorbed by sulfur dioxide. The IR radiation absorbed during combustion of the sample is proportional to the sulfur dioxide in the combustion gases and therefore to the sulfur in the sample. The method is empirical, and SRM's with sulfur percentages in the range of the samples to be analyzed should be used to calibrate the instrument before use.

B. Forms of Sulfur

Sulfur occurs in coal both as organic sulfur and in inorganic combinations such as pyrite, marcasite, and

sulfates. The proportion of these two forms vary widely between different coals and depend to some extent on the total sulfur content.¹² The organic sulfur is chemically combined with the coal organic matter in various functional groups primarily as aliphatic and thiophenic sulfur. Aliphatic sulfur exists as thiols and sulfides. The inorganic sulfur is a small amount of sulfate, mainly in the forms of gypsum ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$) and ferrous sulfate ($\text{FeSO}_4 \cdot n\text{H}_2\text{O}$). In fresh coals the amount is normally small, but it may be more plentiful in oxidized or weathered coals. Pyrite and marcasite are two different crystal forms of FeS_2 , which generally is not uniformly distributed in the coal. It may be disseminated as very fine crystals throughout the organic material or it may occur as layers or slabs in the coal.

Organic sulfur and pyrites account for almost all the sulfur in coals. Sulfate sulfur is usually less than 0.1%, except for weathered coal containing an appreciable amount of pyrites. The relative amounts of pyritic and organic sulfur vary widely. In some coals the total sulfur is almost entirely organic and in others the reverse is true. In Illinois coals organic and pyritic sulfur occurs, on an average, in approximately equal amounts. However, relative amounts vary greatly in individual coals, with both pyritic and organic sulfur ranging from 20 to 80 percent of the total. The pyritic sulfur content varies considerably more than does the organic sulfur content and is of more interest in coal utilization because it is the form that can be most easily

removed from coal by current preparation practices. The main uses of forms of sulfur data are in connection with the efficiency of the cleaning of coal, the inclusion of the pyritic sulfur value in the formula for the estimation of oxygen by difference, and as a possible means of predicting the extent of weathering of coal.¹

The forms of sulfur in coal are determined by ASTM Method D 2492,¹³ "Test Method for Forms of Sulfur in Coal," Figure 2 and Figure 3, in which the sulfate sulfur is determined by extracting coal with dilute hydrochloric acid. The sulfate is precipitated with BaCl_2 , and the BaSO_4 is determined gravimetrically. The determination of pyrite sulfur is carried out using dilute nitric acid as an extraction solution. The concentration of iron in the extract is determined by atomic absorption spectrophotometry or by a titration procedure. The organic sulfur is taken as the difference between the total sulfur and the sum of the sulfate and pyritic sulfur, which cannot be removed from coal by specific gravity separation methods.

Over the decades, methods for the determination of forms of sulfur have been investigated extensively. J.K. Kuhn and coworkers¹⁴ developed the lithium aluminum hydride method. The sulfate sulfur and non-pyritic iron was removed with dilute hydrochloric acid. The pyrite was extracted with lithium aluminum hydride in tetrahydrofuran. The organic sulfur was determined in the extracted residue. The determined organic

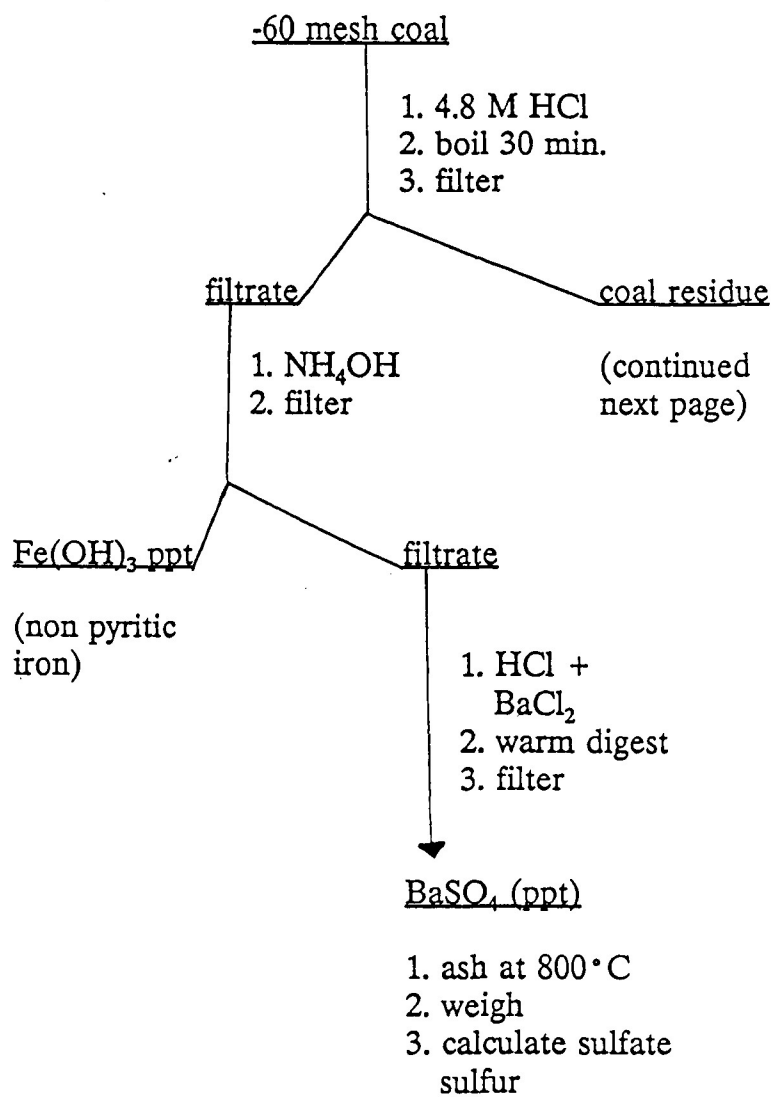
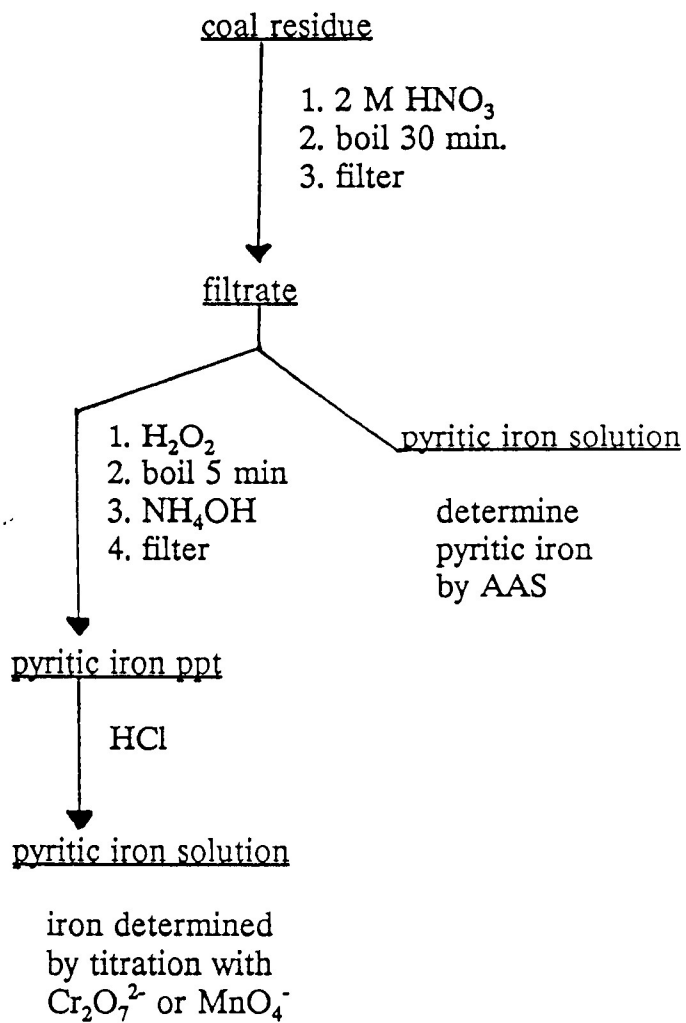


Figure 2. ASTM Method D 2492.



Assume pyritic iron is equivalent to the pyritic sulfur.

$$S_{\text{organic}} = S_{\text{total}} - (S_{\text{sulfate}} + S_{\text{pyritic}})$$

(All values must be reported on the same basis.)

Figure 3. ASTM Method D 2492 (continued).

sulfur values were 0.2-0.3% lower than the calculated ASTM organic values.

C.W. McGowan and R. Markuszewski¹⁵ determined various strengths of perchloric acid (HClO_4) as selective oxidizing agents to determine the sulfate, sulfide, pyritic, and organic sulfur in coals.

W.E. Straszheim and coworkers¹⁶ used scanning electron microscopy-energy dispersive x-ray spectrometry (SEM-EDX) to determine organic sulfur. This method agrees well with ASTM Method D 2492.

C. Solvent Extraction

Solvent extraction is a method for the separation of materials of different chemical types and solubilities by selective solvent action. It utilizes the fact that some materials are more soluble than others in certain solvents, which results in preferential extraction. Bringing solid samples into the liquid phase opens up the possibility of many lines of investigation that can hardly be performed with solids: chromatographic separation and molecular weight determination become feasible; high-resolution NMR becomes easier and more informative; better resolved infrared bands free of scattering by particles are obtainable.

The investigation of a coal's preferential extractability is an important prerequisite to obtain better characterization of the original coal structure. The solubility properties of coal are important in the technique

of solvent extraction. It involves dissolving coal in a solvent to make a coal slurry, which is filtered free from the insoluble material to give the filtrate and leave the residue. The solvent is then recovered from the filtrate to yield the coal extract, which can be used extensively as a convenient method in the study of the organic structure of coal and for the chemical characterization of coal.¹⁷

Coal extraction has been a major focus of interest for over a century. De Marsilly¹⁸ was one of the first researchers to investigate coal solubility by employing various solvents.

The common organic solvents (benzene, ethanol, chloroform, and acetone) do not extract or solubilize more than a few percent by weight of any normal coal, even with the very prolonged Soxhlet extraction recommended by Vahrman.¹⁹ Thus, the azeotropic mixture of benzene and ethanol, the mixture of pyridine and ethylene diamine, the mixture of pyridine and carbon disulfide, and the azeotropic mixture of chloroform, methanol, and acetone have been widely studied.²⁰⁻²²

The significant effect that pyridine has in solubilizing certain coals was first reported by Bedson.²³ Extractability with pyridine and subsequent fractionation of the extract with chloroform were extensively investigated by Wheeler and his school in connection with their theories of coking and of coal structure.²⁴⁻²⁶ Dryden²⁷ identified a number of liquids which he termed specific solvents for coals. These liquids include pyridine and other heterocyclics such as piperidine and morpholine (but not piperazine, pyrrole, or dioxane). They

also include aliphatic compounds with two or more primary amine groups, notably ethylenediamine. Much of the work using these solvents was carried out on bituminous coals of Carboniferous or Permian age; most of them were from Britain,^{28,29} Australia,³⁰ or the United States.^{31,32} Extractability is greatest for coals of 86-88% C (dry, mineral-matter free or dmmf basis) and in pyridine or ethylenediamine may be in the range 20-40%. Lower rank coals may show 5-10% extractability in pyridine and yields fall off very sharply by about 90% C.

Interesting and useful as they may be, the specific solvents are difficult or impossible to remove completely from the residue or extract, as studies using labeled solvents have shown.³³ Some success was achieved in the removal of retained pyridine by supercritical fluid extraction with carbon dioxide.³⁴

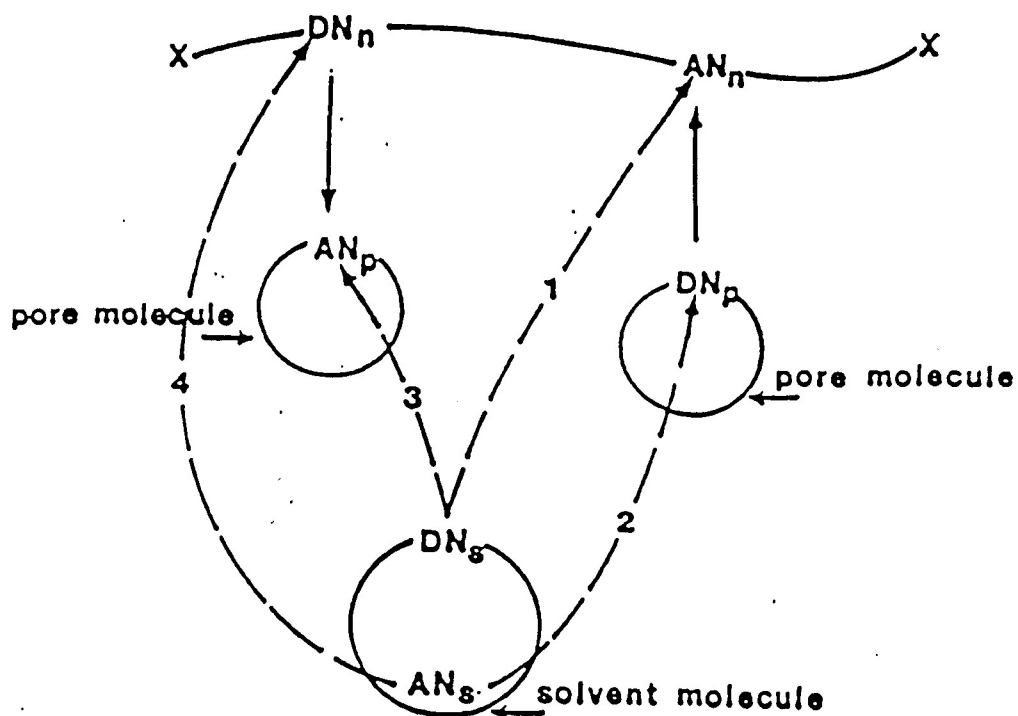
The principle of supercritical fluid extraction of coals is to treat the solute with solvent above the critical temperature of the solvent. The amount solubilized, vaporized with solvent, can be 10-1000 times greater than the amount solubilized in the liquid at subcritical temperatures. Supercritical fluid extraction of coals with toluene at 350°C and about 95 atm (9.7 MPa) affords 30% extract or more if hydrogen or hydrogen donor solvent is present.³⁵

Bartle and coworkers³⁵⁻³⁷ made detailed studies of the products of extracting some high-volatile bituminous coals and two lignites from Turkey with supercritical toluene. Over 60%

of the extract was soluble in benzene (atmospheric pressure) but insoluble in hexane, while the balance was either soluble in hexane or insoluble in benzene. The products were fractionated in various ways, and the fractions examined by ^1H and ^{13}C NMR. The results were interpreted in terms of distributions of hydrogen and carbon in different types of combination and expressed as mean numbers of atoms of each type per average molecule.

The interesting observations were made that if a coal is first swollen by exposure to the vapor of a polar solvent, the extractability with another polar solvent is decreased, whereas the extractability with a nonpolar or weakly polar solvent is usually increased by the same treatment.³⁸

Although over a century's investigations on various aspects of coal extraction have been done, details on the mechanism still remain somewhat ambiguous. The electron donor and acceptor bond formation model suggested by Marzec and coworkers^{39,40} is considered important in explaining the performance of various solvents for coal extraction at ambient temperature. They used the concepts developed by Gutman,⁴¹ which quantitatively describe intermolecular phenomena in terms of interactions between electron donors and electron acceptors. The model for coal extraction (Figure 4) put forward by Marzec and coworkers envisaged both electron donors and electron acceptors as present in the insoluble network of coals and also in the smaller extractable molecules which are a matrix of macromolecules filling the coal pores. The donor-



DN: the electron donor number;

AN: the electron acceptor number;

1, 2, 3, and 4: possible routes of donor/acceptor bond formation between solvent molecules and electron donor or acceptor centers of coal.

Figure 4. Coal extraction model.^{39,40}

acceptor bonds between the extractable molecules themselves or between extractable and network are replaced by solvent-extractable bonds. Accordingly, solvents that are to give good extraction yields should have both their donor and acceptor numbers in the proper ranges.

Solvents with an unshared electron pair on nitrogen or oxygen are frequently called specific solvents,²⁷ which are able to selectively dissolve a substantial amount of coal at temperatures near or below the normal boiling point of the solvent. Those solvents extract the material in the capillary system as well as material weakly bonded to the polymer matrix, which results in the breaking of hydrogen bonds, acid-base complexes, etc. They also cause coal to swell which may improve extraction efficiency.

Pyridine, one of the specific solvents, has been extensively employed as an extraction solvent for the study of the organic structure of coal. The extraction is highly rank dependent, reaching approximately 20% for a low-rank bituminous coal, yielding a peak value around 88.5% carbon, then decreasing to zero at 92% carbon.

Pyridine is a basic, polar, nucleophilic solvent. It tends to solubilize organic materials by breaking some of the weaker interactive bonding molecules to the coal matrix. Infrared spectroscopy has shown that the organic materials extracted closely resemble the organic compounds making up the polymer matrix.⁴²

Dimethylformamide, DMF, is a highly polar, aprotic solvent. Ekoterinina and coworkers⁴³ concluded for DMF extraction that the extraction yield is dependent on the content of active acid groups and changes in accordance with the stage of coalification and the hydrogen bonds that exist between the solvent and certain structural groups in the coal.

Tetrahydrofuran, THF, is one of the oxygen containing heterocyclic specific solvents. It is extensively used in coal extraction.

These specific coal solvents have been widely used in coal extraction and in the determination of organic sulfur in the extracts. Buchanan and coworkers⁴⁴ studied the sequential extraction of pristine Illinois No. 6 coal, APCSP-3, with toluene, tetrahydrofuran, dimethylformamide, and pyridine, in which they concluded that the extract yield was 28% (by weight) and the organic sulfur in the extract was 29%. Calkins^{45,46} reported that tetrahydrofuran was superior to acetonitrile, ethylenediamine, and pyridine for the extraction of organic sulfur from a Pittsburgh No. 8 bituminous coal.

D. Organic Sulfur Compounds in Coal

Organic sulfur exists in coal as aliphatic sulfur and thiophenic sulfur. Aliphatic sulfur is in the form of sulfides, thiols, and disulfides. Thiophenic sulfur is composed of sulfur-heteroatomic rings such as thiophenes, benzothiophenes, and thiozanthenes. Thiophenic sulfur is the most difficult of the organosulfur compound to remove from

coal. The identification of organic sulfur compounds in coal and its extracts has been extensively investigated by numerous researchers over the past two decades.

Yurovski⁴⁷ employed a classical approach to determine the types of organosulfur compounds in alcoholic solutions of phenol extracts of coal. In the study with a Russian coal, Yurovski determined that about 48% of the organosulfur compounds in the coal were thiophenic in nature, while the remaining organosulfur compounds consisted of a mixture of thiols, sulfides, and maybe disulfides.

G.N. George and coworkers⁴⁸⁻⁵⁰ used a bulk technique, x-ray absorption near-edge structure (XANES), for the direct speciation and approximate quantification of organically bound forms of sulfide and thiophenic sulfur in coal. They concluded that a lignite they studied contained $30 \pm 10\%$ sulfidic and $70 \pm 10\%$ thiophenic sulfur, and an Illinois No. 6 coal contained $60 \pm 10\%$ sulfidic and $40 \pm 10\%$ thiophenic sulfur.

Huffman and coworkers^{51,52} used a surface technique, x-ray photoelectron spectroscopy (XPS), to study the structures of sulfur groups in several bituminous coals. They concluded that the organic sulfur compounds in bituminous coals are predominantly thiophenic in nature.

R.E. Winans and coworkers⁵³ determined the organic sulfur compounds in the Argonne Premium Coal Samples and a set of three macerals from a Lewiston-Stockton coal by ion source, desorption/pyrolysis high resolution mass spectrometry. The

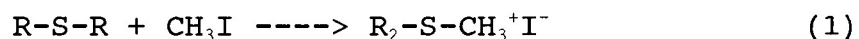
data they obtained correlated with XANES and XPS very well, from which they concluded that specific structural assignments to the sulfur species can be made.

Traditional coal Soxhlet extraction is a time-consuming method which takes about two days and leaves excessive organic solvent waste. Peter K.K. Louie and coworkers⁵⁴ developed a rapid and reproducible method to quantify elemental sulfur in coal by using supercritical fluid extraction and gas chromatography with atomic emission detection. This method requires only a 30 minute extraction and produces a minimum of waste solvent. They concluded that as much as 35.7% of the organic sulfur defined by ASTM is elemental sulfur rather than organic sulfur. The elemental sulfur correlates well with the inorganic sulfur fractions of coal. The total amount of elemental sulfur extracted is independent of the coal particle size, and similarity in extraction rates from three coal particle sizes indicates that elemental sulfur in coal is located at the surface of the coal particles.

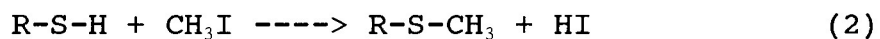
The standard ASTM D 2492 technique for the determination of sulfur forms in coal measures specific forms of sulfur while ignoring others. Only total and sulfate sulfur are measured directly. Pyritic sulfur in coal is estimated based on iron content, and the organic sulfur is presently estimated by difference. According to the ASTM D 2492 guidelines, elemental sulfur in coal is currently counted as organic sulfur -- a significant source of error for the determination of sulfur forms in coal.^{55,56}

The reaction of sulfur functional groups with selective reagents has been moderately successfully in solid coal analysis. Angelova and Syskov⁵⁷, Angelova⁵⁸, Baranskii and coworkers⁵⁹, as well as Gundermann and coworkers⁶⁰ exploited several methods of sulfur methylation to estimate -SH, -SR, and -S-S- structures by treating coal with methyl iodide and then extracting sulfur as the trimethylsulfonium iodide. They indicated that -SH, -SR, and -S-S- groups could account for as much as 90% of the total organic sulfur, although they usually appeared to encompass only 5-15% in coals with low-to-moderate sulfur contents.

Postovski and Harlampovich⁶¹ used methylation by methyl iodide to estimate the amount of sulfidic sulfur in accord with the reaction as:



Determination of the amount of I^- left in the sample is a measure of the concentration of organic sulfides. Mercaptans and thiophenols release HI when reacted with CH_3I :

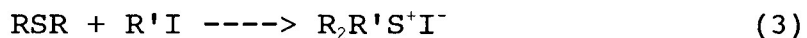


where R is neither aliphatic nor phenyl group. The HI released thus can be used to estimate the amount of -SH groups in the sample.

Bogdanova and Boranski,⁶² as well as Prilezhaeva and coworkers⁶³ developed this method to evaluate the organic sulfur functional group distribution in coal. The data suggest that in bituminous coals, the organic sulfides constitute some 5-20% of the organic sulfur, whereas the rest is assumed to be thiophenic. About 70% of the sulfidic sulfur is in an unstable form. Thiophenic, condensed thiophenic, and aryl sulfides do not react with CH_3I .

Rose and Francisco⁶⁴ developed the isotopic trace method to analyze the acidic thiols. They employed ^{13}C -isotopic methyl iodide reacting with thiols in a strong environment. Then they used an NMR technique to identify the isotopic methylated products. This technique is only useful for thiols. It does not work with sulfides and thiophenic sulfur.

Due to the excellent nucleophilicity of sulfur, sulfides and thiophenic sulfur are involved in the alkylation yielding sulfonium ions as indicated by the equations:^{65,66}



where the sulfur in RSR is either aliphatic sulfur or thiophenic sulfur.

In the reaction the silver tetrafluoroborate (AgBF_4) is employed to precipitate the competitive nucleophile, iodide. The rate of reaction is dependent on the nucleophilicity of sulfur of which aliphatic sulfides is faster than thiophenic sulfur. The less reactive sulfur compounds may be alkylated

by using trialkyloxonium tetrafluoroborates or adding alkyl halides in the presence of silver salts.^{67,68}

The typical ¹³C NMR chemical shift ranges for methyl groups are shown in Figure 5. The methylsulfonium cation appears around 20 ppm to 40 ppm. Table 1 presents ¹³C NMR chemical shifts for a series of methylsulfonium model compounds. Reactions of sulfur methylation to form sulfonium salts can be demonstrated with a number of model compounds.⁶⁹

Attar and coworkers⁷⁰⁻⁷³ used thermokinetic analysis to determine the proportions of thiolic, thiophenolic, aliphatic sulfides, aryl sulfidic, and thiophenic sulfur in five coals. In this method the kinetics of the nonisothermal hydrolysis of coal was followed. H₂S was released from different functional forms in different temperature ranges and monitored with the aid of an H₂S-specific detector such as that used on a gas chromatograph. A plot of rate of release of H₂S against temperature or time at constant heating rates showed a series of peaks. The area of these peaks was proportional to the amount of each functional form present. A careful analysis of the nonisothermal kinetics was presented to justify the procedure. These researchers estimated that 15-30% of the organic sulfur in coal is sulfidic, while 30-55% of the organic sulfur in lignite and 40-60% in bituminous coals is thiophenic. The remaining organic sulfur is assumed to be thiolic in nature.

Thermogravimetric analysis (TGA) is a technique in which a sample is continuously weighed as it is heated at a

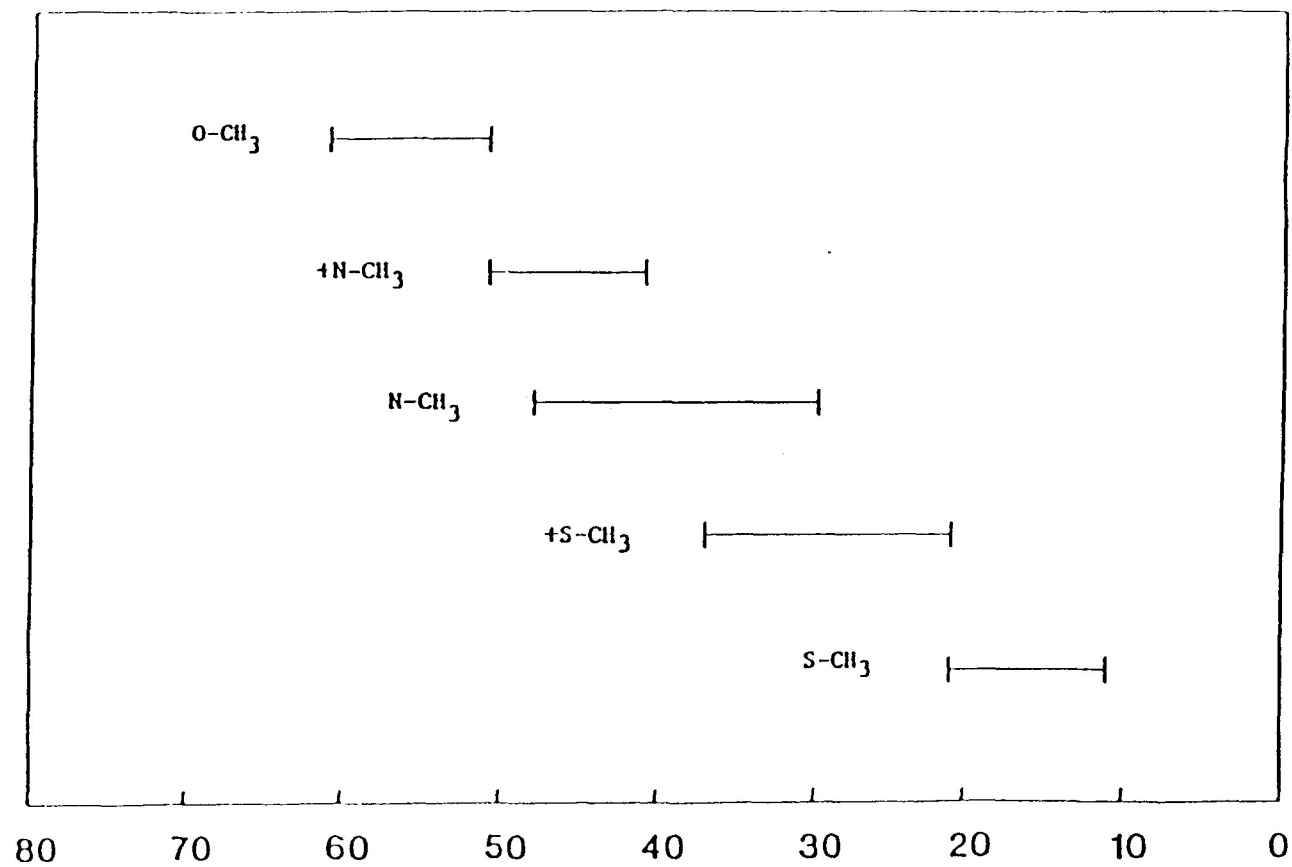
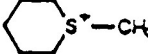
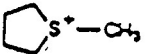

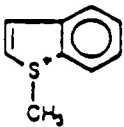
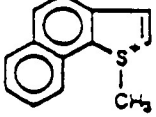
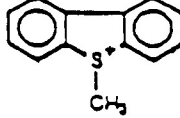
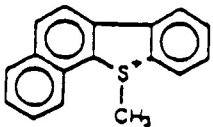


Figure 5. ^{13}C NMR chemical shift ranges for methyl groups (ppm).

Table 1. ^{13}C NMR Chemical Shifts
of Methylsulfonium Model Compounds

$\text{CH}_3\text{CH}_2\text{S}^+\text{CH}_2\text{CH}_3$ CH_3	21.0
$n\text{Bu}-\text{S}^+-n\text{Bu}$ CH_3	22.7
$\text{PhCH}_2\text{S}^+\text{CH}_2\text{Ph}$ CH_3	21.7
	22.2
$\text{PhCH}_2\text{S}^+\text{Ph}$ CH_3	25.3
	25.9
$\text{PhS}^+\text{CH}_2\text{CH}_3$ CH_3	26.1
PhS^+Ph CH_3	28.4
PhS^+CH_3 CH_3	29.3
	28.3
	31.7
	31.2
	34.9
	34.2

constant, preferably linear, rate. The temperatures and amounts of evolved components or breakdown products can be determined based on the TGA weight loss curve.

Coupling the TGA and a fourier transform infrared spectrometer (FTIR) allows the identification of the evolved gases that relate to the specific TGA weight loss. A thermogravimetry-fourier transform infrared (TG-FTIR) system collects the gas infrared data from thermal analysis at an integral temperature. Aliphatic sulfur and aromatic sulfur in coal can be oxidized to sulfur dioxide in air at different temperatures. TG-FTIR shows the absorbance peaks at the temperature at which the sulfur dioxide is formed. Aliphatic sulfur is easily oxidized at low temperature. The pyritic sulfur peak appears following the aliphatic sulfur peak. The stable thiophenic sulfur is finally oxidized at higher temperature.⁷⁴

Chapter II

EXPERIMENTAL

A. Reagents and Instrumentation

The raw coal 90008 used in this research was a Herrin, IL No. 6 seam, high volatile bituminous C (hvCb) coal. Calibration standards for the analysis of carbon, hydrogen, nitrogen, and sulfur were National Institute for Standards and Technology (NIST) and LECO coal calibration standards. The N,N-dimethylformamide, 99+% spectrophotometric grade, the tetrahydrofuran, the iodomethane 99%, the acetonitrile 99.5% spectrophotometric grade, the acetonitrile-d₃ 99.5 atom % D, the methyl sulfide anhydrous 99+%, the 4-methoxybenzyl chloride 98%, the benzyl mercaptan 99%, the 4-methoxy- α -toluenethiol technical 90%, the nitromethane 99+%, the 1,2-dichloroethane 99+%, the tetrabutylammonium hydroxide 40 wt % were from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. The silver tetrafluoroborate 99% was from Johnson Matthey Company, Ward Hill, Massachusetts. The iodomethane-¹³C 99 atom % ¹³C was from Sigma Chemical Company, St. Louis, Missouri and Aldrich Chemical Company, Milwaukee, Wisconsin.

The Isotemp Vacuum Oven, Model 281, was from Fisher Scientific in Pittsburgh, Pennsylvania. The 16PC FTIR and the atomic absorption spectrometer 3100 were from Perkin Elmer in

Norwalk, Connecticut. The LECO CHN-1000, LECO SC-432, and LECO TGA-501 were from the LECO Company in St. Joseph, Michigan. The JNM-GSX 270 FT-NMR was from JEOL LTD in Tokyo, Japan. The Rotavapor was from Brinkman Instruments, Westburg, New York. TG-FTIR runs were made on a TA 951 TG system and Perkin Elmer 1650 FTIR. GC/MS runs were made with a Hewlett-Packard 5890A Gas Chromatograph-5970 Series Mass Selective Detector system.

B. Procedures

Carbon, hydrogen, and nitrogen contents in all samples were determined using a LECO CHN-1000 analyzer. Sulfur in all samples was determined with a LECO SC-432 sulfur analyzer. The solids from the coal DMF and THF extracts were sent to Shimadzu Instrumentation Company to perform mass spectrometry identification.

1. Determination of Forms of Sulfur

A 2 g sample of -60 mesh coal was mixed with 50 mL of HCl (2 volumes of concentrated HCl + 3 volumes of water). The mixture was gently boiled for 30 minutes. After filtering and water-washing, 10 mL of 30% H_2O_2 was added to the filtrate to oxidize all inorganic sulfur forms to sulfate ions and ferrous ions to ferric ions. The solution was boiled to remove excess H_2O_2 . The iron was precipitated with excess ammonia and filtered. Barium chloride was added to the filtrate to precipitate BaSO_4 . After filtering the precipitate, the filter paper was placed in a crucible, burned at $800 \pm 25^\circ\text{C}$, and

this temperature maintained overnight. After cooling and weighing, the percentage of sulfate sulfur was calculated as:

$$\text{Sulfate sulfur \%} = \{[(S - C_s) - (B - C_B)] * 13.735\}/W \quad (4)$$

where S = weight of sample crucible plus ignited BaSO_4 precipitate; C_s = weight of sample crucible; B = weight of blank crucible plus ignited sulfate blank; C_B = weight of blank crucible; and W = weight of test portion used.

The filter paper and HCl extracted residue were mixed with 50 mL of HNO_3 (1 volume of concentrated HNO_3 + 7 volumes of water), and the mixture boiled gently for 30 min., or left overnight to oxidize iron species to iron (III) and inorganic sulfur compounds to sulfate. After filtering, the filtrate was saved for the determination of iron by atomic absorption spectrophotometry. The percentage of pyritic sulfur was calculated as:

$$\text{Pyritic sulfur, \%} = [F * A * V * C * P * (T - B)]/W \quad (5)$$

where F = 1.148, dimensionless, the stoichiometric ratio of sulfur to iron in iron disulfide (FeS_2); A = 25, dimensionless, the aliquot factor indicating proportion of filtrate used to prepare to the test solution; V = 100 mL, the volume of the test solution; C = 10^{-6} g/ μg conversion factor; P = dimensionless, conversion factor from weight fraction to percentage by weight; T = concentration of iron in the test

solution, $\mu\text{g/mL}$; B = concentration of iron in the blank test, $\mu\text{g/mL}$; and W = weight of the test portion.

2. DMF or THF Extraction

DMF and THF extractions were conducted in triplicate with standard Soxhlet extractors. The Soxhlet was insulated by glass wool wrapped in aluminum foil to prevent heat loss. The procedure is as follows:

- a. Dry 100 mL beakers at 100-110°C (1 hr.), cool down in a desiccator, and weigh to the nearest mg.
- b. Weigh 10 g of -60 mesh raw coal, place it in a vacuum oven at 60 \pm 4°C for a period of six hours. After the temperature has dropped to less than 50°C (to prevent rapid air oxidation), remove coals to desiccator, cool to room temperature and reweigh to obtain moisture loss.
- c. Concurrently with step b, mark cellulose Soxhlet thimbles, vacuum dry with the coal, cool in desiccator, and weigh. Transfer the dry coal samples to the thimbles and weigh again.
- d. Set up the Soxhlet extraction apparatus units, load the coal-containing thimbles, add 150 mL of DMF or THF in the 250 mL flask. Insulate the glass assembly below the condenser so that most of the heat loss occurs in the condenser. Keep the reflux extraction going 20 to 24 hours.
- e. Collect the DMF or THF extract from flasks. Add 150 mL of methanol to flasks, reassemble, and carry out reflux rinsing of the coal residue for 5-6 hours.

f. Remove Soxhlet thimbles, allow free solvent to drain away and air dry the coal residues. Place in vacuum desiccator, evacuate for about 30 minutes, and let stand overnight.

g. Transfer to vacuum oven and dry at 150°C for a period of six hours. Allow temperature to drop to less than 50°C, remove the coal residues to cool in desiccator, and weigh to obtain extraction loss.

h. Replace the coal residues in vacuum oven and dry at 150°C for two hours. Allow temperature to drop to less than 50°C, remove the coal residues to cool in desiccator and weigh. Repeat this step until constant weight is obtained.

3. Determination of Moisture and Ash

A 1 g sample of -60 mesh coal, or DMF and THF extract residues, is loaded into the LECO TGA-501 Analyzer crucible. The analysis is done automatically.

4. S-Methylation and ^{13}C NMR Spectroscopy

A 1 g sample of coal or THF extract was added to 30 mL of THF and stirred under nitrogen for 30 min. One mmol of aqueous solution tetrabutylammonium hydroxide was then added and stirred under nitrogen for 30 min. Two mmol of methyl iodide was added and the mixture was stirred under nitrogen at room temperature for two days. THF and methyl iodide were removed by rotovaporization under reduced pressure. The residue was washed with a hot 50/50 volume of methanol/water mixture until the filtrate was free of iodide (no precipitate

with silver nitrate) and tetrabutylammonium ion (no precipitate with sodium tetraphenylborate). The product was dried under vacuum at 50°C for 24 hours. To the product was added 3 mL of DCE and five mmol of methyl iodide and the mixture stirred. Four mmol of AgBF_4 was dissolved in 2 mL of DCE and was added to the mixture by syringe. The reaction solution was stirred for 12 hours under nitrogen. The AgI was removed by centrifugation and washed by acetonitrile. The solvents were removed by rotovaporization.

The final product was re-dissolved in acetonitrile- d_3 . The nitromethane was used as an internal standard. ^1H NMR spectra were run under a pulse width of 5.2 μs and a pulse delay of 3 μs . ^2H NMR spectra were run under a pulse width of 3.0 μs and a pulse delay of 1 μs . ^{13}C NMR spectra were run under a pulse width of 2.6 μs and a pulse delay of 3 μs . For quantitative determination of ^{13}C -enriched product, $\text{Cr}(\text{OCOCH}_3)_3$ was added and the ^{13}C NMR spectra were run under a pulse width of 2.6 μs and a pulse delay of 1 μs .

5. Reaction of Model Sulfide Compounds

The 4-methoxybenzyl sulfide was made by mixing equal amounts of 4-methoxybenzyl chloride and 4-methoxy- α -toluenethiol in CH_3CN and then heated and refluxed for 12 hours. Ethanol was used as a recrystallization solvent. The structure of the product was confirmed by GC/MS spectroscopy.

The 4-methoxybenzyl benzyl sulfide was produced by the same procedure as the 4-methoxybenzyl sulfide. These two sulfides plus methyl sulfide were subjected to sulfur

methylation by methyl iodide with or without the presence of AgBF_4 as described in procedures 4.

6. Fourier Transform Infrared Spectrometry

All the samples including coal 90008, the DMF and THF extract residues, and the solids after taking off DMF or THF from the extracts were analyzed by FTIR spectroscopy. One part of sample was mixed with 100 parts finely powdered potassium bromide. After grinding, a pellet was made for running the FTIR spectrum.

7. TG-FTIR

A 15 mg portion of sample was loaded into the TGA weighing pan. The sample was heated at the rate of $10^\circ\text{C}/\text{min}$ from 25°C to 800°C in air. The weight loss during heating was recorded at every 10°C .

A 150 mg portion of sample was loaded into the TGA weighing pan. The heating rate was $10^\circ\text{C}/\text{min}$ from 25°C to 800°C . The absorbance was recorded every 10°C .

Chapter III

RESULTS AND DISCUSSION

A. Coal Extraction

The structure of dimethylformamide is such that the oxygen of the carbonyl can form a good O---H bond and the nitrogen is connected by two electron donating methyl groups, which makes it easier for the lone pair electron on nitrogen to accept hydrogen to form a hydrogen bond. On the other hand, the oxygen of tetrahydrofuran has ring restriction. The total effects of electronegativity, attached groups, and the steric structure results in the formation of stronger hydrogen bonds in the DMF extracts compared to those in the THF extracts. The yields of extraction shown in Table 2 indicate that the percent of extraction of coal in DMF is higher than that in THF, which matches the structure characteristics of the solvents. These characteristics are also illustrated by the decreases in the percentages of carbon and hydrogen in the extracts. With the removal of organic species by solvents, the percentage of mineral matter in extract residues increases, which results in the increase of the percentage of ash in the extract residues.

The percentages of total sulfur, pyritic sulfur, and sulfate sulfur are higher in extract residues than in raw

Table 2. Analytical Data for Raw Coal 90008, DMF
and THF Extracted Coal 90008

	Raw Coal 90008 ^{A, B}	DMF Extract Residue ^{A, B}	THF Extract Residue ^{A, B}
% Extraction	-	26.91	17.17
% Moisture	9.35	0.35	0.59
% Ash	17.88	22.74	20.45
% Carbon	78.56	72.09	77.42
% Hydrogen	5.61	3.99	4.76
% Nitrogen	1.17	4.90	1.46
% Oxygen	9.38	12.57	10.04
% S Organic	2.59	2.26	3.31
% S Pyrite	2.66	4.05	3.02
% S Sulfate	0.03	0.14	0.04
% S Total	5.27	6.44	6.37

^A Ash is expressed on a dry basis.

^B All values other than moisture and ash are expressed on a dry, ash-free basis.

coal. This higher percentage occurs because the good extractability increases the mineral substances in extract residues. Due to the better extractability of DMF compared to THF, the percentages of total sulfur, pyritic sulfur, and sulfate sulfur in DMF extract residues are higher than those in the THF extract residues.

Although the analytical data for solids from the coal 90008 extracts, as shown in Table 3, are expressed on an as-determined basis and can not be accurately compared with the data of raw coal and extract residues, which are based on a dry, ash-free basis, the percentages of nitrogen, oxygen, and sulfur in extracts are still very high. The increases of the contents of carbon, hydrogen, and oxygen show that the organic components are extracted by these organic solvents. The decreases in the percentages of sulfur result from the fact that the pyritic sulfur and sulfate sulfur are insoluble in these organic solvents.

Comparisons of raw coal with the DMF and THF extracts can be made on the basis of atomic ratios, as shown in Table 4. The ratios of hydrogen-to-carbon for the coal and the solids from the extracts differ very little (0.01 and 0.03), an indication that the aromatic carbon in the extracts changes little from that in the raw coal. The small difference in hydrogen-to-carbon ratio between the DMF and THF extracts shows the aliphatic polar solvents have the same extractability on the aliphatic components of the coal. The data for oxygen-to-carbon ratios show that the more polar

Table 3. Analytical Data for Solids From Raw
Coal 90008 DMF and THF Extracts^A

	Solid in DMF Extract	Solid in THF Extract
% Carbon	78.47	81.81
% Hydrogen	5.50	6.02
% Nitrogen	1.60	1.13
% Sulfur	2.42	2.37
% Oxygen	12.01	8.67

^A All values are expressed on an as-determined basis.

Table 4. Atomic Hydrogen-to-Carbon (H/C), Organic Sulfur-to-Carbon (S_{org}/C), Total Sulfur-to-Carbon (S_{tot}/C), Nitrogen-to-Carbon (N/C), and Oxygen-to-Carbon (O/C) Ratios

	Raw coal 90008 ^A	DMF Extract Residue ^A	THF Extract Residue ^A	Solid from DMF Extract ^B	Solid from THF Extract ^B
H/C	0.85	0.66	0.73	0.84	0.88
S_{org}/C	0.012	0.012	0.016	ND	ND
S_{tot}/C	0.025	0.033	0.031	0.012	0.011
N/C	0.013	0.058	0.016	0.017	0.012
O/C	0.089	0.13	0.097	0.11	0.080

^A Expressed on a dry, ash-free basis.

^B Expressed on an as-determined basis.

^C ND = Not determined.

solvent DMF extracted more oxygen-containing groups than the less polar solvent THF. These data show that the ratios of total sulfur-to-carbon in extracts are different from those in the parent coal by differences of 0.013-0.014.

Fourier transform infrared (FTIR) spectroscopy is potentially one of the most versatile techniques available for providing analytical data on raw materials, the process chemistry and the products. The FTIR spectra permit rapid routine qualitative and quantitative characterizations of solids, liquids, and gases.

The FTIR spectra of raw coal 90008, its extract residues and the solids from the extracts, as shown in Figure 6 and Figure 7, consist of complicated overlapping peaks. The strong water absorption near 3400 cm^{-1} is superimposed on the O-H and N-H stretching bonds in these spectra. The broad band near 3400 cm^{-1} for raw coal, the DMF extract residue, and the THF extract residue are for the major phenolic OH groups, as shown in Figure 1.

The broadening of the hydroxyl band near 3500 cm^{-1} in the solids from the DMF and THF extracts is due to the formation of $\text{N}\cdots\text{H}$ and $\text{O}\cdots\text{H}$ hydrogen bonding, respectively. In all the spectra, the aliphatic C-H stretch and aromatic C-H stretch appear between 3100 cm^{-1} and 2800 cm^{-1} ; the strong band near at 1600 cm^{-1} is due to aromatic ring stretching; the strong band at 1450 cm^{-1} is methylene and methyl bending. The bands between 1000 cm^{-1} and 1100 cm^{-1} , which are shown in coal and its extract residues, seem to be the C-O single bond stretch

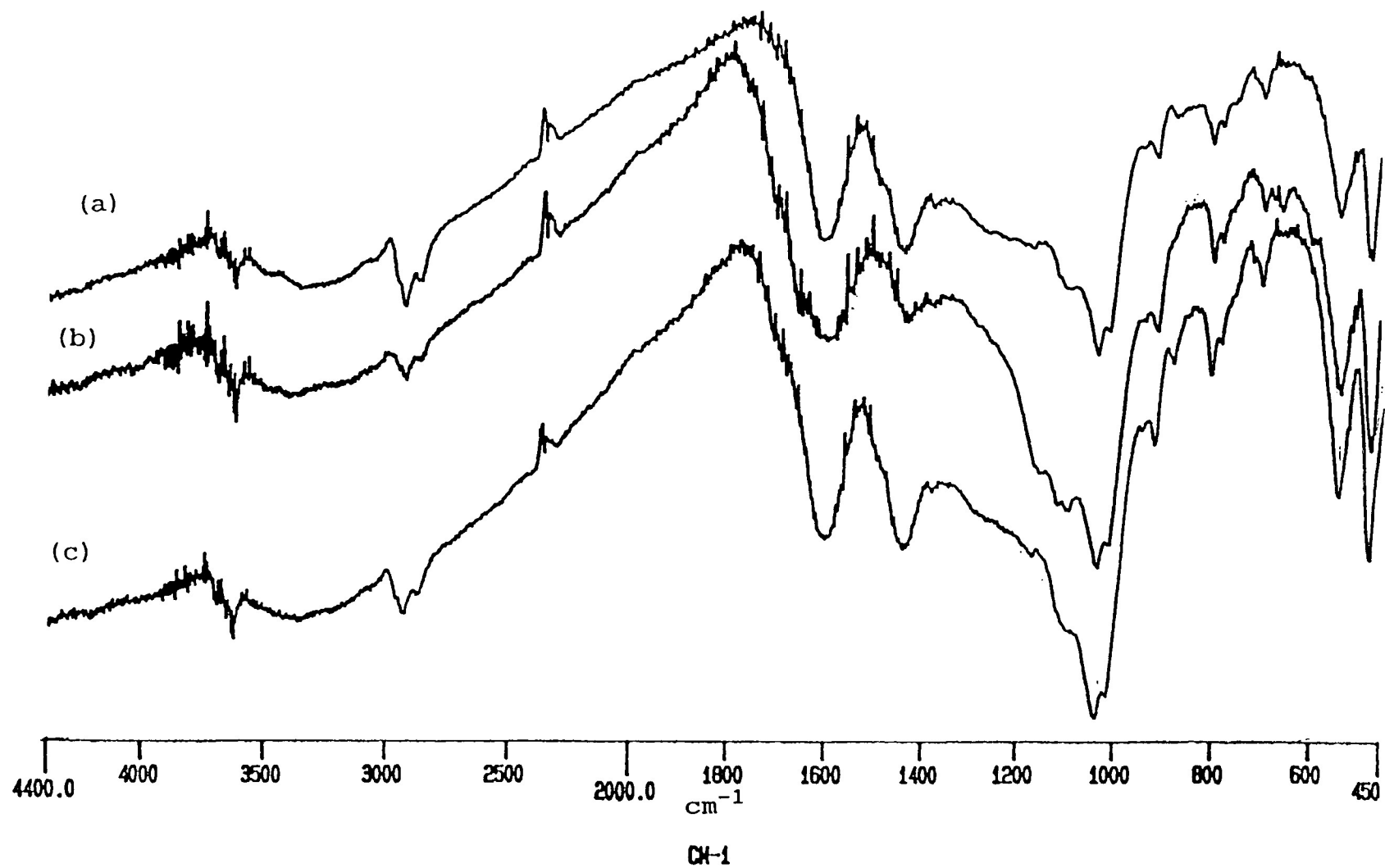


Figure 6. FT-IR spectra of (a) coal 90008, (b) coal DMF extract residue, and (c) coal THF extract residue.

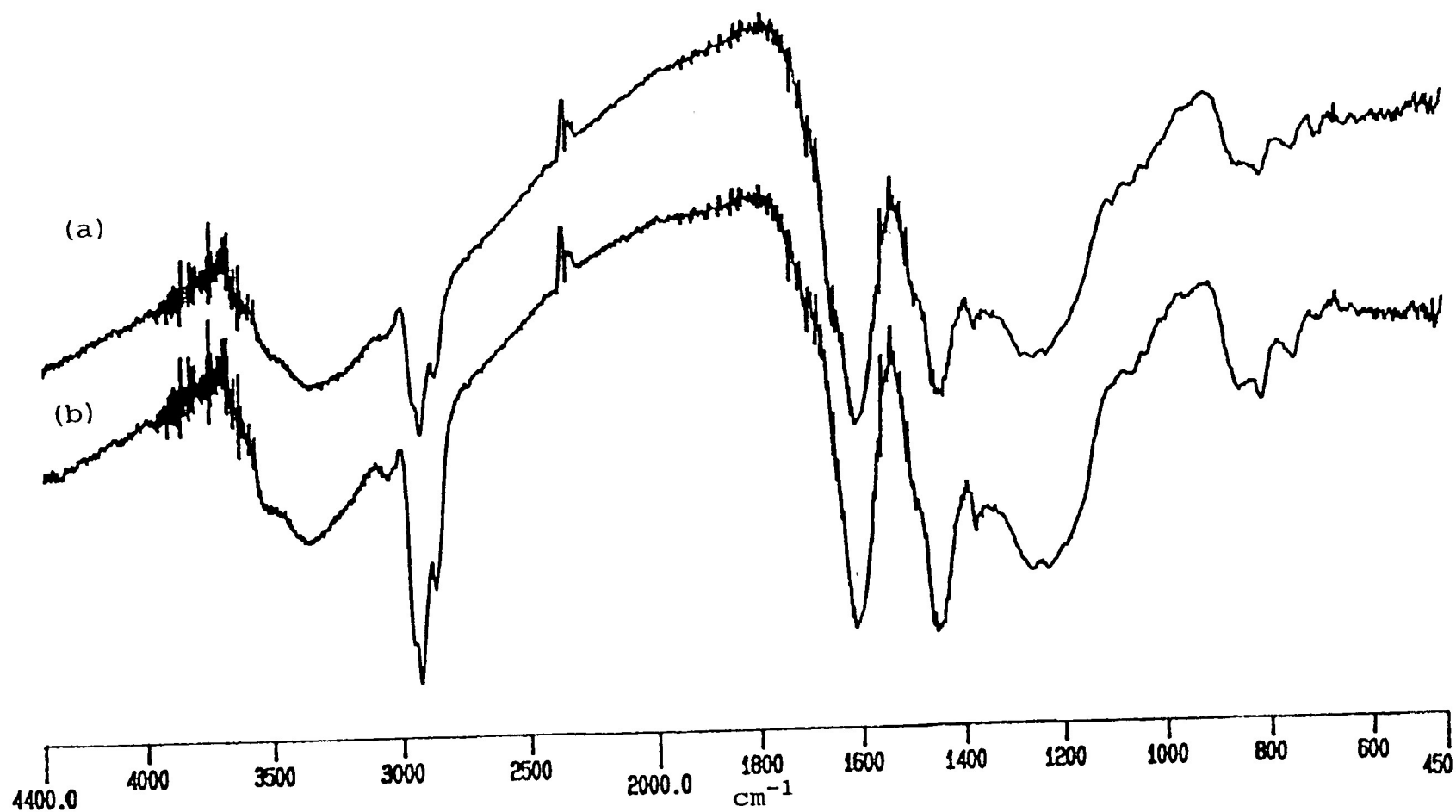


Figure 7. FT-IR spectra of (a) the solid from the coal DMF extract, and (b) the solid from the coal THF extract.

of aliphatic ethers and alcohols, or the bands of mineral matter. The disappearance of these bands in solids from the extracts indicates the bands are from mineral matter -- that is to say, the extracts are enriched in organic materials. The bands between 700 cm^{-1} and 900 cm^{-1} may be the aromatic C-H out-of-plane bending modes.

In Figure 7 the spectrum of the solid from the DMF extract of the coal shows the weak shoulder at 1650 cm^{-1} , which supports the results from the carbon, hydrogen, and nitrogen determinations in that DMF is hard to remove completely. The broad band at 1250 cm^{-1} shown in Figure 7 is due to the C-O stretch or C-N stretch, which may result from the extract solvent remaining or from the fact that these stretches are covered up by the mineral bands in raw coal.

The FTIR spectra of the raw coal, DMF and THF extract residues, and the solids from extracts are quite similar. This similarity might be reasonably representative of the parent coal structure in all these samples.

The mass spectrometry data for the solids from the coal extracts indicate that the solids are composed of a number of complicated organic species. Because of the heterogenous complex characteristics of coal, the identification of these species needs the combination of mass spectrometry data with several other techniques, the results of which may reveal the organic structure of coal in the future.

B. Thermal Analysis of Sulfur in the Coal Extracts

Sulfur in coal exists as inorganic sulfur both as pyritic and sulfate sulfur and also as organic sulfur both as aliphatic and thiophenic sulfur. These forms of sulfur can be oxidized to sulfur dioxide at different heating temperatures. Thermogravimetric analysis (TGA) is one of the techniques to determine the weight loss during the oxidation. Figures 8 and 9 show that moisture loss occurred at 261°C and 276°C from the solids from the DMF and THF extracts, respectively, which are possibly the result of impurities. Over 99% of the sample was oxidized when the temperature reached 550°C.

The sulfur dioxide eluted at different oxidation temperatures is then detected by the FTIR instrument. Figure 10 shows the sulfur dioxide absorbance versus temperature for the THF and DMF extracts of coal 90008, indicating that sulfur dioxide eluted from aliphatic sulfur oxidation around 325°C and from thiophenic sulfur oxidation around 480°C for the DMF extract and 580°C for the THF extract.

As observed in Figure 10, aliphatic sulfur is oxidized at 325°C. Raw coal 90008 was preheated at 350°C to remove all the aliphatic sulfur then extracted by THF to study the results of sulfur oxidation. After the THF solvent was rotovaporized, the residue solid was run on the TG-FTIR instrument. The spectrum of this residue is shown in Figure 11. The absorbance peak at 325°C did not appear, thereby providing evidence that the aliphatic sulfur is oxidized at 325°C.

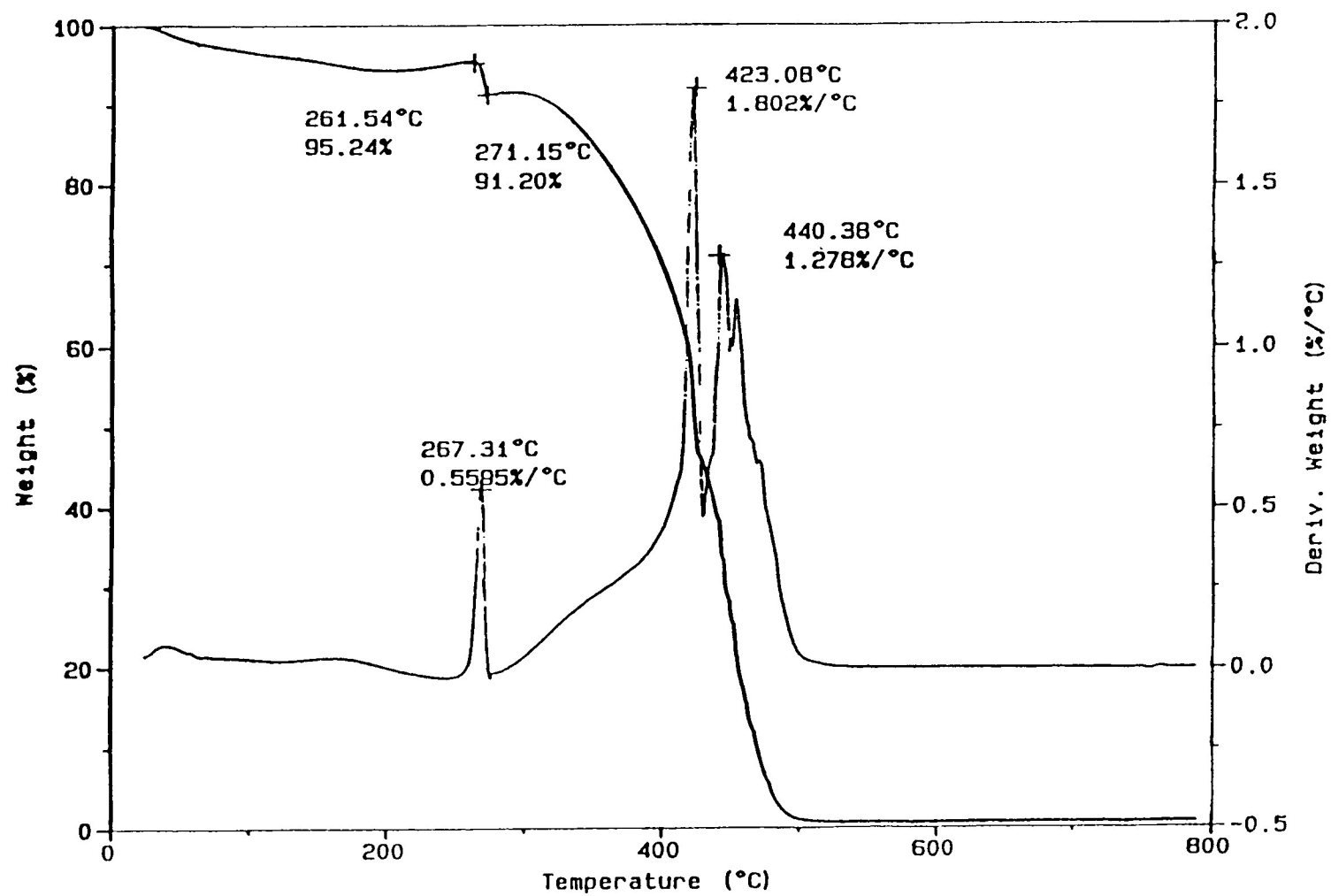


Figure 8. TGA weight loss curve for the solid from the coal DMF extract.

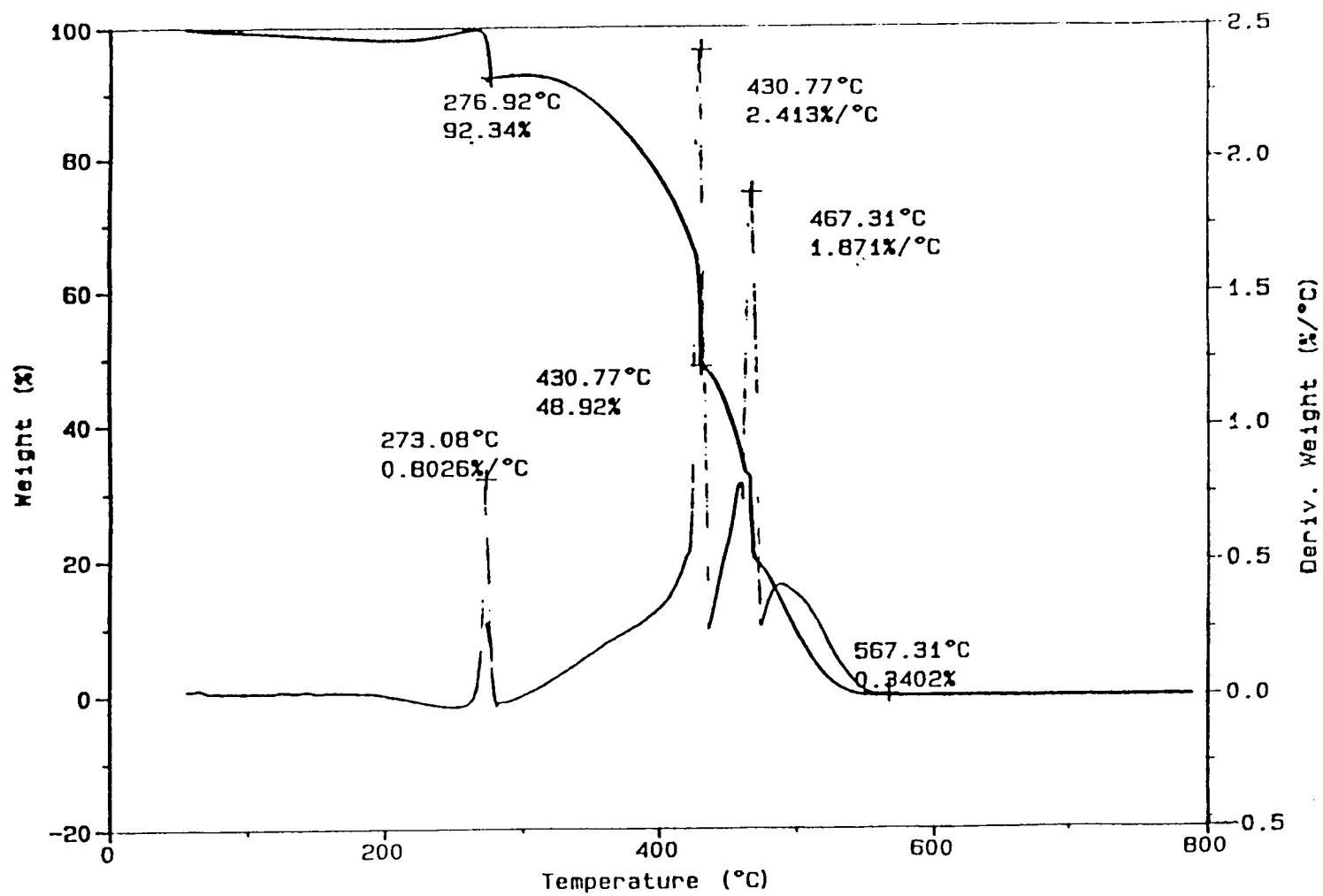


Figure 9. TGA weight loss curve for the solid from the coal THF extract.

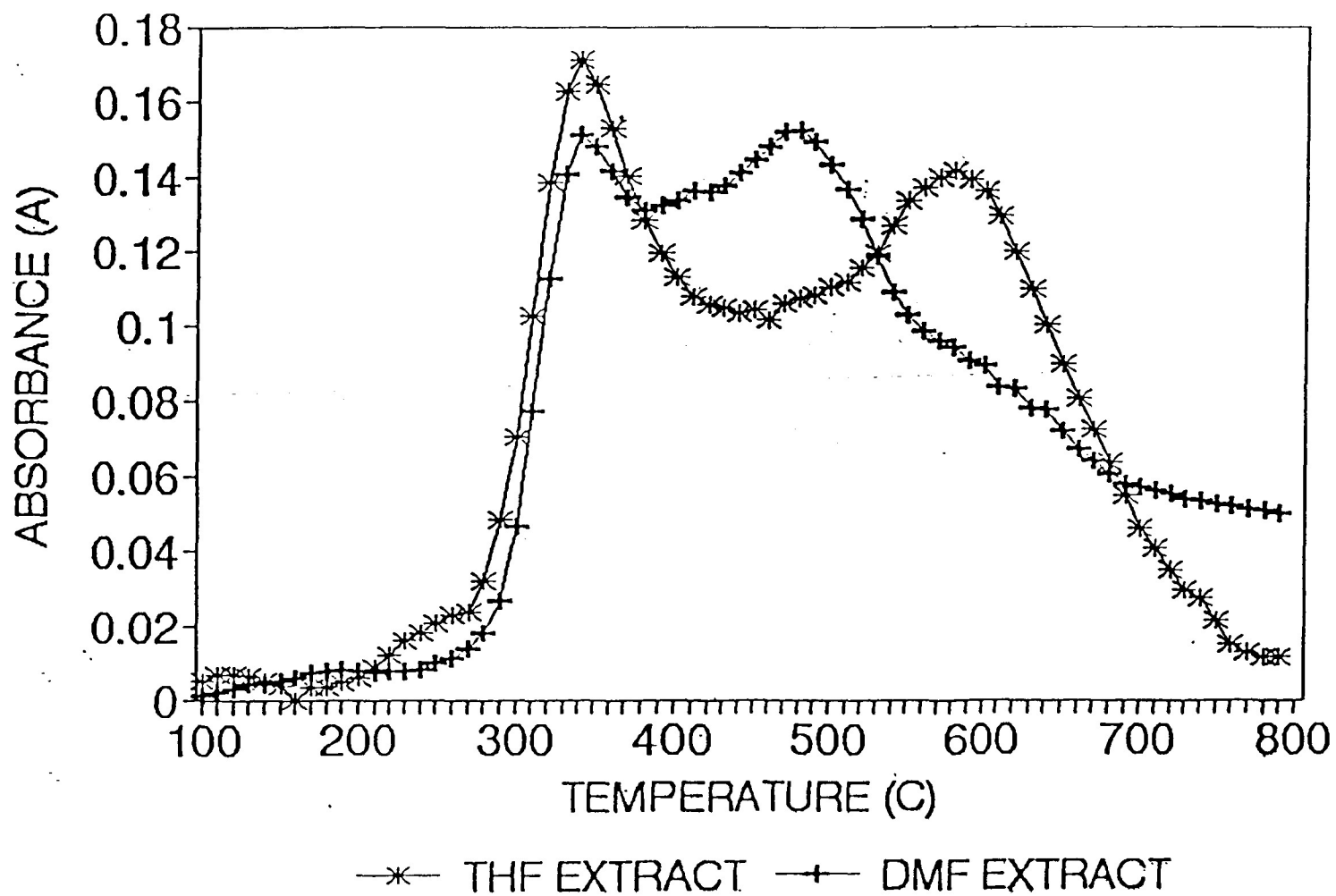


Figure 10. TG-FTIR spectra of SO_2 absorbance vs. temperature for the solids from the coal extracts heated in air.

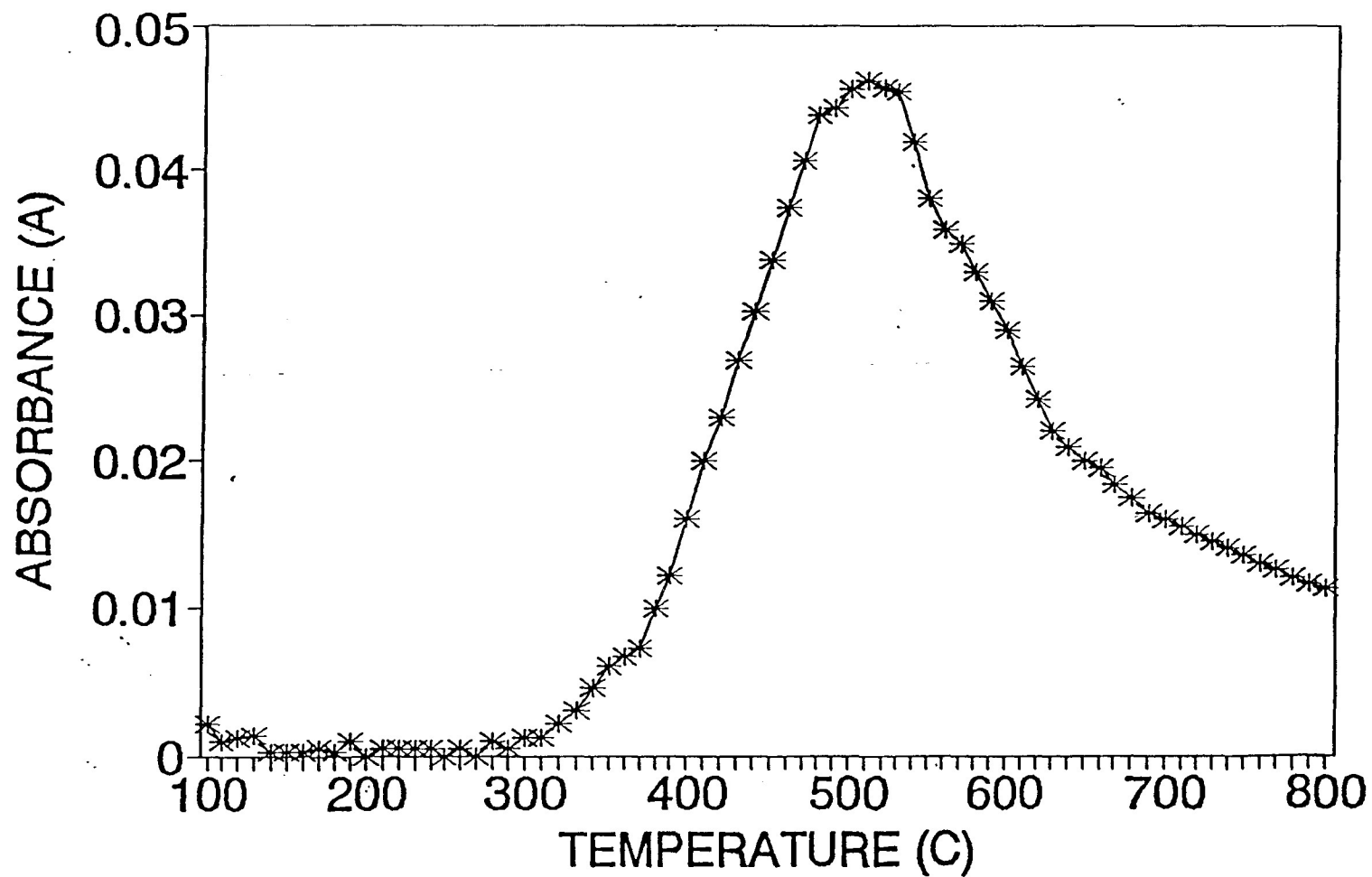


Figure 11. TG-FTIR spectra of SO_2 absorbance vs. temperature for raw coal 90008 preheated at 350°C in air.

C. Organic Sulfur Species in Coal and its Extracts

Organic sulfur species in coal exist as aliphatic and thiophenic sulfur in which the aliphatic sulfur exists mainly as sulfides. Table 5 shows the components of forms of sulfur in raw coal, which is based on the assumption that aliphatic and thiophenic sulfur are oxidized at different temperatures. The data indicate that there is a higher percentage of aliphatic sulfur in raw coal 90008 than in thiophenic sulfur.

Both aliphatic and thiophenic sulfur can be methylated with polar solvents and silver tetrafluoroborate. As the model coal structure in Figure 1 shows, the oxygen in coal and coal THF extracts exists primarily as phenol functional groups. Tables 2 and 3 show that the raw coal and the THF extract have 9.38% (dry, ash-free basis) and 8.67% (as-determined basis), oxygen respectively.

We attempted to identify organic sulfur species by reacting the sulfur with an isotopically-labelled reagent, followed by NMR analysis. In this case we converted sulfur compounds to methyl sulfonium salts by reacting the sulfur compounds with methyl iodide in the presence of silver tetrafluoroborate. This reaction is a nucleophilic substitution reaction which produces an ionic product, a reaction that is favored in a polar solvent. Dichloroethane(DCE) is often employed in this kind of sulfur methylation. The methyl iodide is labelled either with deuterium, in which case ^2D NMR is used for analysis, or with

Table 5. Forms of Sulfur in Raw Coal 90008^A

Coal 90008	A. ASTM D 2492; ASTM D 4239	B. ASTM D 4239; Forsythe Method ⁷⁴	% Total Sulfur
Organic Sulfur	2.13	2.27	A. 49.19 B. 52.42
Pyritic Sulfur	2.18	2.04	A. 50.35 B. 47.11
Sulfate Sulfur	0.02	N/A	0.46
1. Total Sulfur	4.33	N/A	N/A
2. 365°C Oxidized Total Sulfur	N/A	2.33	53.81
3. 440°C Oxidized Total Sulfur	N/A	0.29	6.7
Aliphatic Sulfur (1-2)	N/A	2.00	46.18
Thiophenic Sulfur (3-Sulfate Sulfur)	N/A	0.27	6.24

^A All the data are given on a dry basis.

carbon-13, in which case ^{13}C NMR is used for analysis. The results are then compared to those of model compounds.

We chose to first selectively methylate the phenols in the coal or extract with unlabelled methyl iodide. There are two advantages to this approach. First, the phenols will compete with sulfur in the sulfur methylation chemistry, lowering yield of methyl sulfonium salts. Second, methylation of phenols disrupts hydrogen bonding in the coal, leading to better accessibility of the sulfur methylating reagents. The method of Green and coworkers was used for S-methylation,⁶⁹ and the method of Liotta was used for O-methylation.⁷⁵

Raw coal 90008 (Illinois No. 6) and the THF extract were O-methylated first with ^{12}C -iodomethane and then S-methylated with ^{12}C -iodomethane. Figures 12 and 13 show the ^{13}C NMR spectra of these products. Because of the inherent low NMR sensitivities and low natural abundance of ^{13}C , the expected product peaks at the chemical shift range of 20-35 ppm are weak and are hidden by the peaks attributed to the original samples. Thus, ^{13}C -enriched iodomethane was employed in S-methylation in place of ^{12}C -iodomethane. The ^{13}C NMR spectra of these products, shown in Figures 14 and 15, have broad peaks at 20-35 ppm, which are the resonances of methyl sulfonium salts of sulfides and thiophenes. In these spectra a high intensity peak is distinguished at 26.8 ppm for the product from the raw coal and at 27.2 ppm for the product from the THF extract. This peak is tentatively attributed to trimethylsulfonium tetrafluoroborate. To aid in verifying

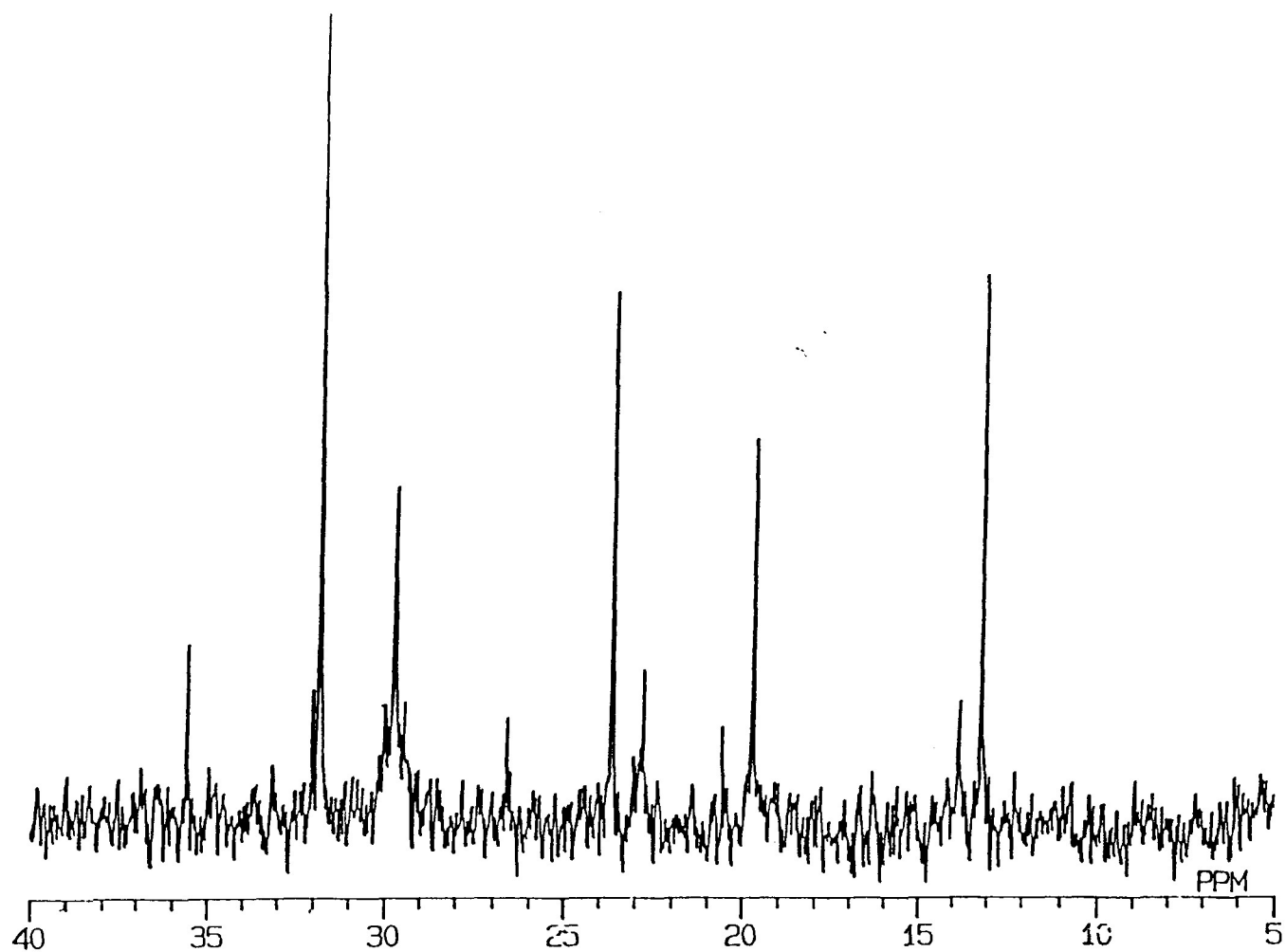


Figure 12. ^{13}C NMR spectrum of methylated raw coal 90008 by ^{12}C -iodomethane in base, then by ^{12}C -iodomethane with AgBF_4 .

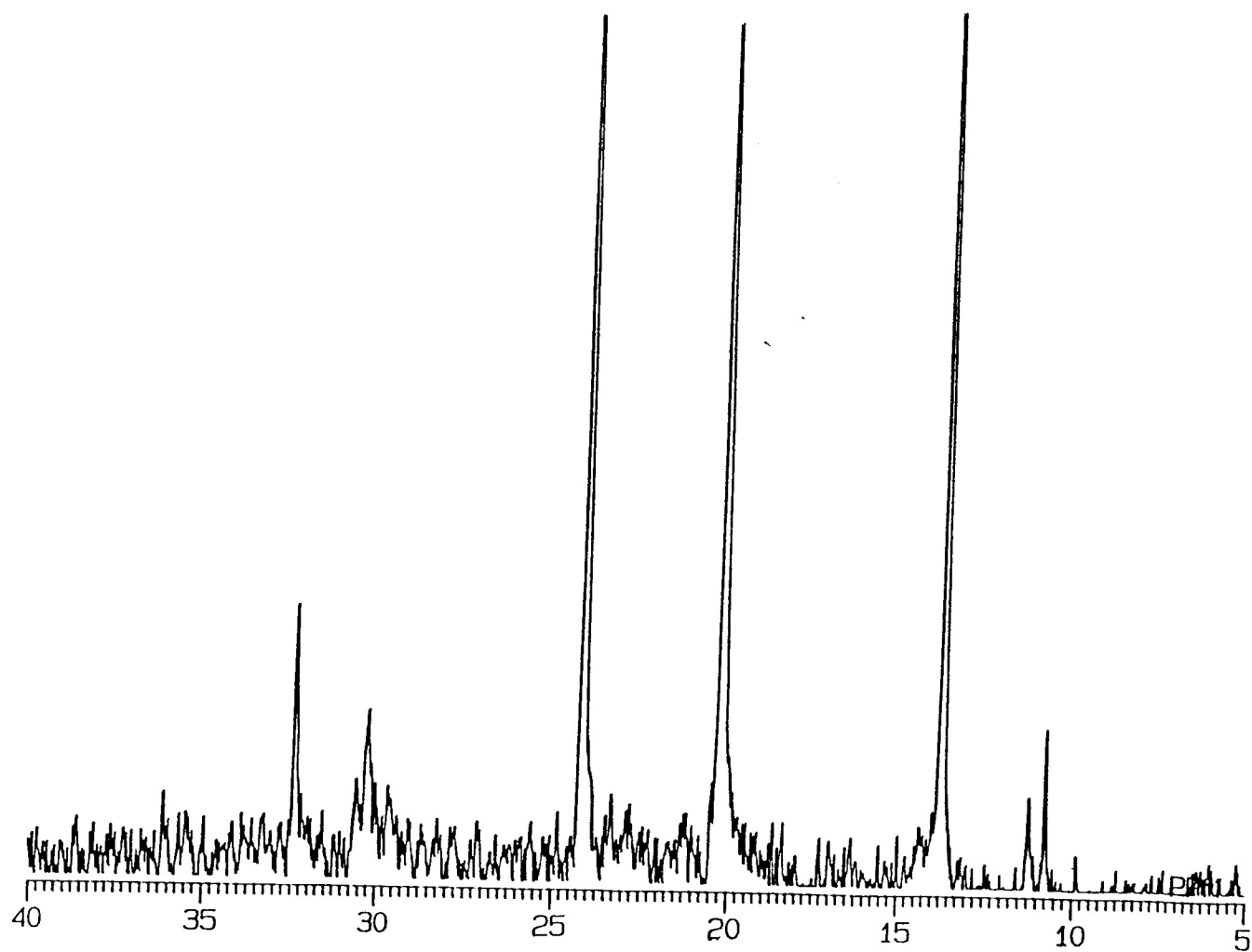


Figure 13. ^{13}C NMR spectrum of methylated solid from the coal THF extract by ^{12}C -iodomethane in base, then by ^{12}C -iodomethane with AgBF_4 .

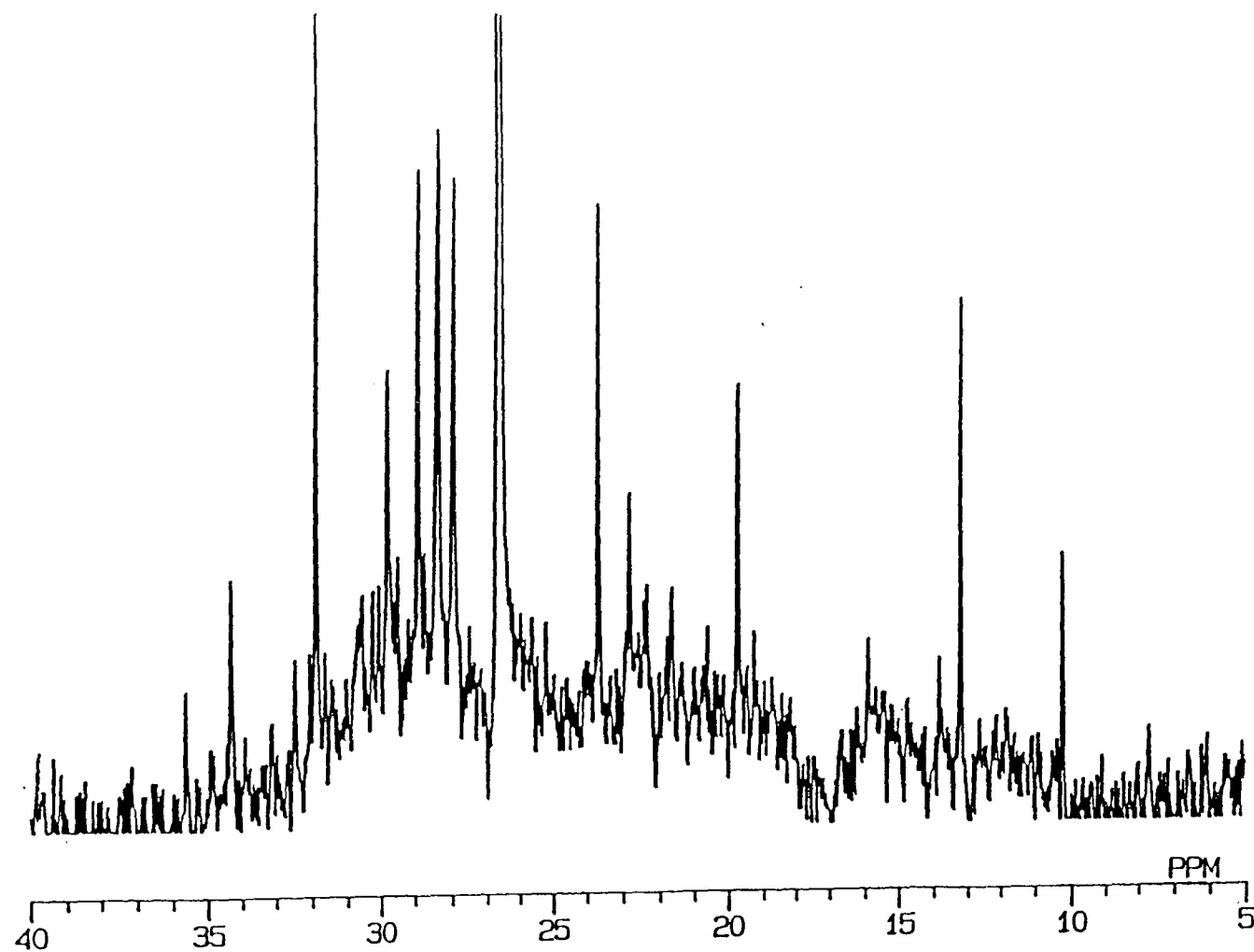


Figure 14. ^{13}C NMR spectrum of methylated raw coal 90008 by ^{12}C -iodomethane in base, then by ^{13}C -iodomethane with AgBF_4 .

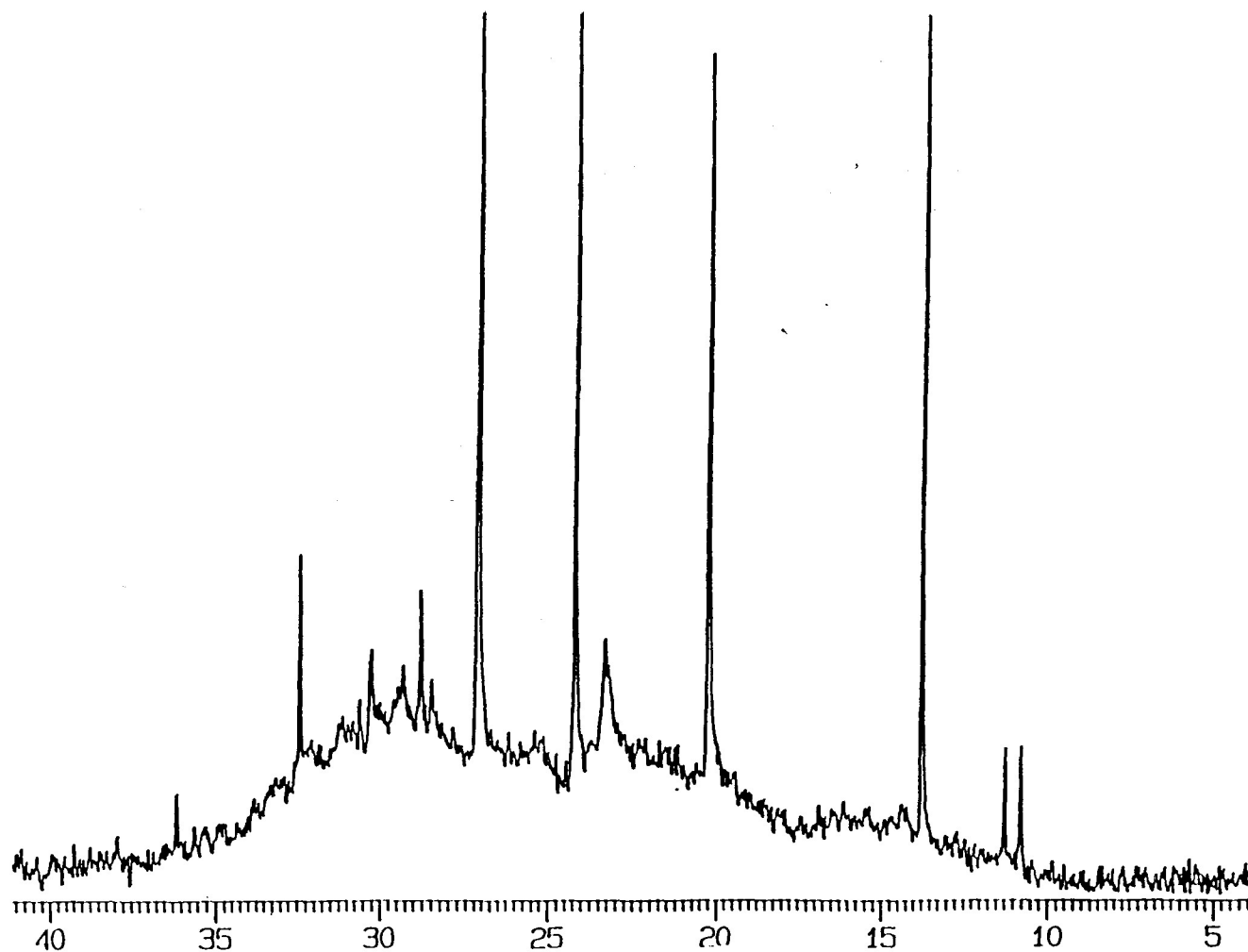


Figure 15. ^{13}C NMR spectrum of methylated solid from the coal THF extract by ^{12}C -iodomethane in base, then by ^{13}C -iodomethane with AgBF_4 .

this product, this model salt (made by methylation of methyl sulfide with iodomethane and AgBF_4) was added to the product from the coal THF extract, and the ^{13}C NMR spectrum was again acquired, as shown in Figure 16. Surprisingly, the spiked and unspiked products have the same resonance at 27.2 ppm. The difference is that the spiked one has a stronger intensity than the unspiked one, further confirming the reaction product, trimethylsulfonium tetrafluoroborate.

The formation of trimethylsulfonium tetrafluoroborate might be attributed to the methylation of methyl sulfide or methyl disulfide in the coal structure. However, neither of these compounds are found in coal, suggesting that carbon-sulfur bonds are being cleaved in the coal to produce this product.

We were not aware of any model sulfur compounds that undergo C-S bond cleavage under these reaction conditions. It seemed reasonable that aliphatic C-S bonds are being cleaved (not thiophenes) and that the C-S bond is somehow activated or weakened by the presence of oxygen functions such as phenols or, in this case, methylated phenols. Therefore, 4,4'-dimethoxydibenzylsulfide and 4-methoxydibenzylsulfide were selected as model compounds for testing this hypothesis. The compound 4,4'-dimethoxydibenzylsulfide was synthesized by reacting 4-methoxybenzyl chloride and 4-methoxybenzylthiol. The product was identified by GC-MS as shown in Figure 17. The m/z ratio of 274 and 121 indicate the parent ion $(\text{CH}_3\text{OPhCH}_2)_2\text{S}^+$ and stable ion $(\text{CH}_3\text{PhCH}_2^+)$, respectively. The

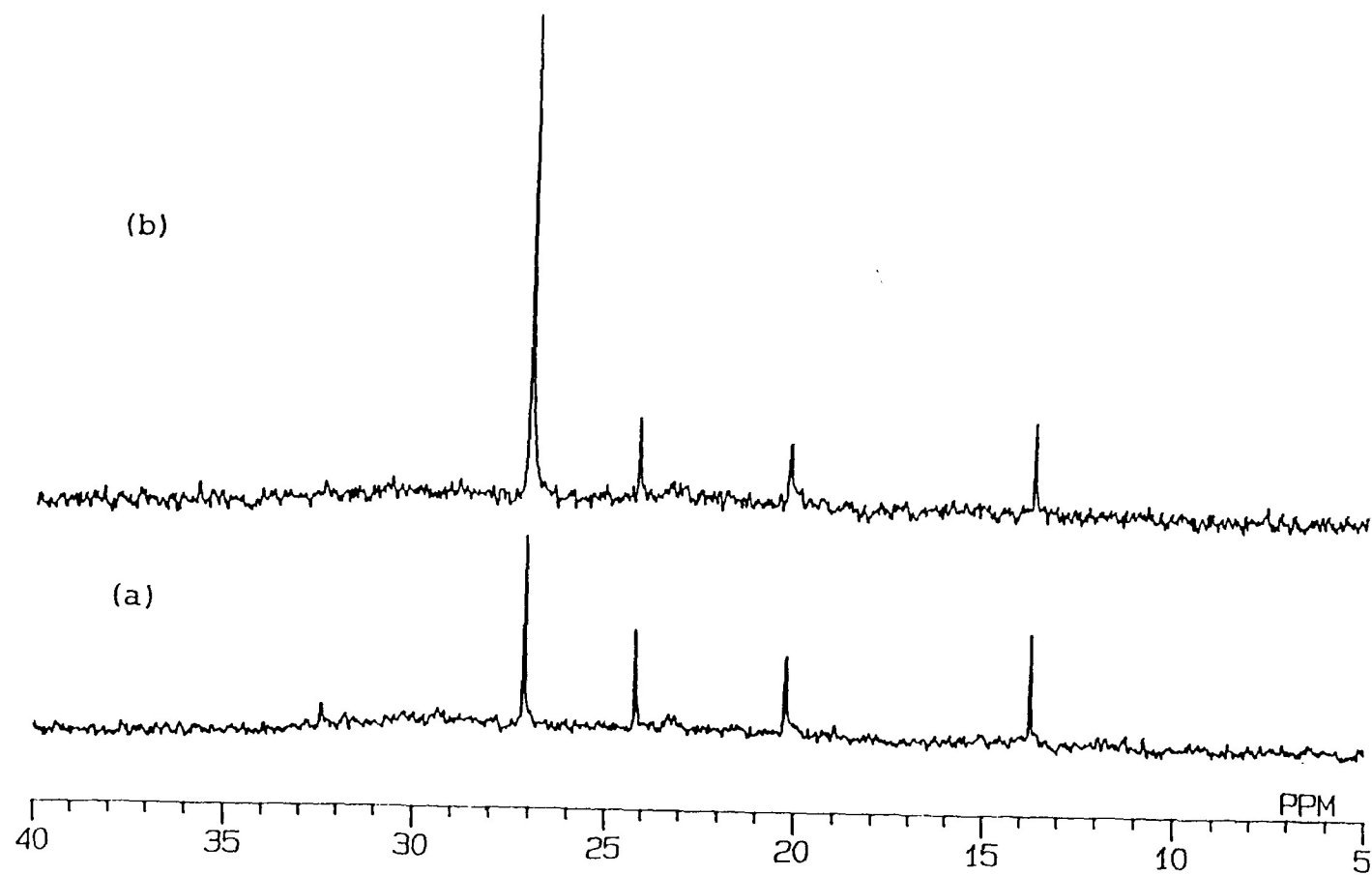
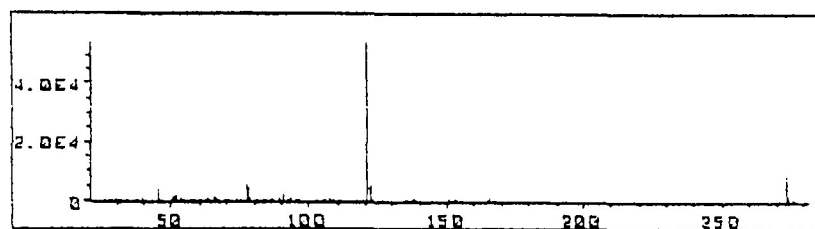


Figure 16. ^{13}C NMR spectra of (a) unspiked product shown in Figure 15, and (b) trimethylsulfonium spiked product shown in Figure 15.



TABULATE

[MS1]

Scan 517 (9.243 min)

Y: Scan 820 (14.161 min) of S

X: Scan 775 (13.443 min) of S

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
38.95	2	65.05	2	107.00	1	165.95	1
44.95	6	77.05	9	109.00	2	197.05	2
49.95	1	78.05	7	121.00	99	227.00	1
50.95	3	79.05	1	122.00	9	228.00	2
52.05	2	89.05	1	138.00	1	274.05	14
53.05	1	91.00	4	150.95	1	275.05	2
55.05	1	94.00	1	152.95	1		

Figure 17. Mass spectrum and m/z ratios of $(\text{CH}_3\text{OPhCH}_2)_2\text{S}$.

other model compound, 4-methoxydibenzyl sulfide, was made in the same way.

The compounds were reacted with iodomethane with and without the presence of AgBF_4 . The ^1H and ^{13}C NMR spectra and assignments are shown in Figures 18-21. A distinguishing phenomenon of the reaction of these compounds in the presence of AgBF_4 is the color change from yellow to brownish red, which indicates the formation of iodine. No significant color change occurred in the absence of AgBF_4 . Also, trimethylsulfonium tetrafluoroborate was observed as a major product from the reaction of 4,4'-dimethoxydibenzylsulfide in the presence of AgBF_4 , as evidenced by the singlet at 2.8 ppm in the ^1H spectrum and at 27.2 ppm in the ^{13}C spectrum. These resonances are absent in the spectra of the products from the reaction without AgBF_4 .

The major product observed when 4-methoxydibenzylsulfide was reacted in the presence of AgBF_4 was dimethylbenzylsulfonium tetrafluoroborate. This product was confirmed by both ^1H and ^{13}C NMR. Assignments are made in Figures 20 and 21. This product indicates that only the C-S bond associated with the 4-methoxybenzyl group is cleaved. It further confirms that the C-S bond must be activated by the methoxy substituent in order to be cleaved. Further work is needed to establish products from methylation of this model in the absence of AgBF_4 . However, it is clear that a different set of products is obtained, making clear that AgBF_4 is necessary for bond cleavage.

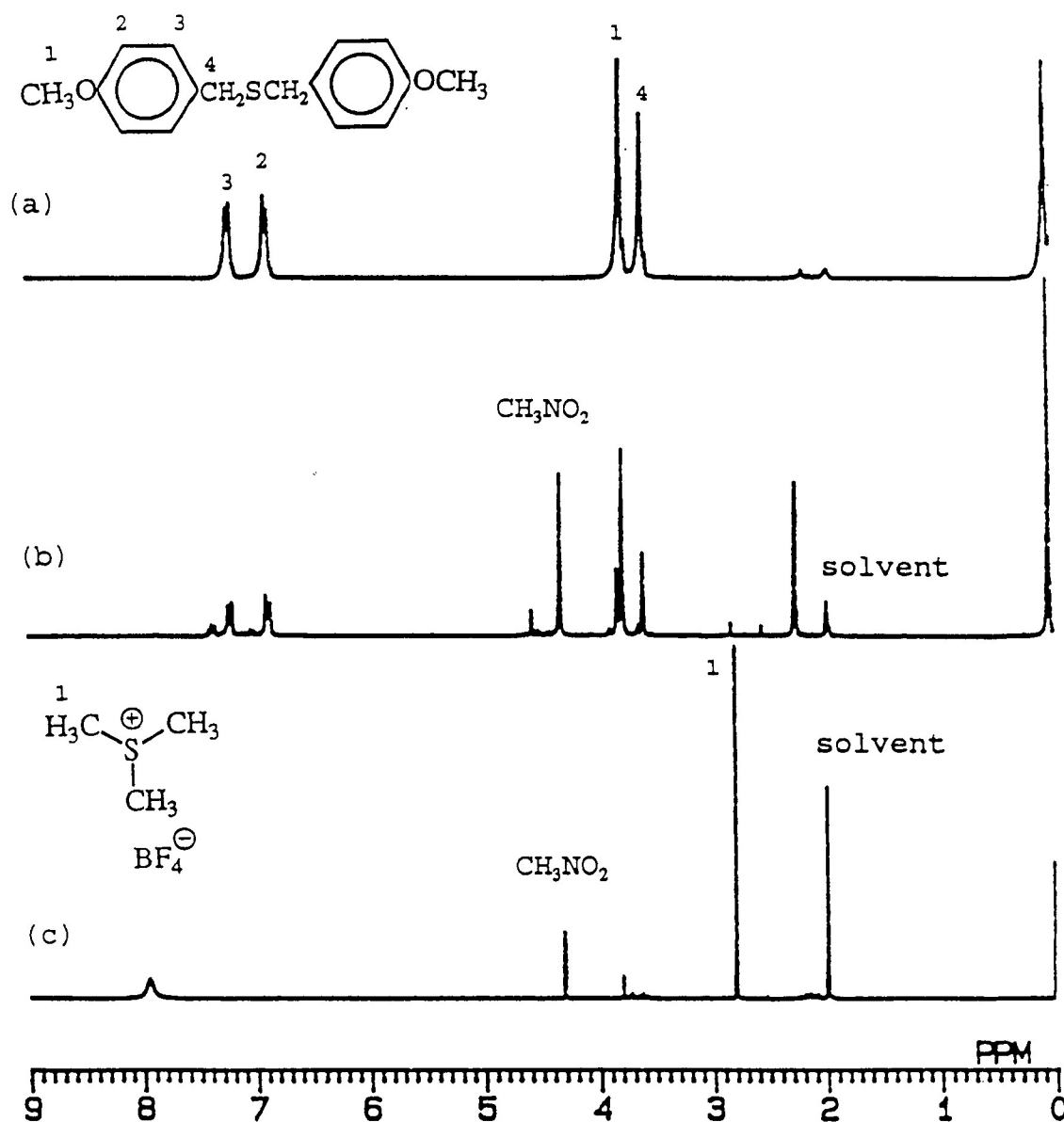


Figure 18. ^1H NMR spectra and assignments of $(\text{CH}_3\text{OPhCH}_2)_2\text{S}$ and its methylated products (CD_3CN as solvent, TMS as reference): (a) $(\text{CH}_3\text{OPhCH}_2)_2\text{S}$, (b) $(\text{CH}_3\text{OPhCH}_2)_2\text{S} + \text{CH}_3\text{I}$ without AgBF_4 , CH_3NO_2 as internal standard, and (c) $(\text{CH}_3\text{OPhCH}_2)_2\text{S} + \text{CH}_3\text{I}$ with AgBF_4 , CH_3NO_2 as internal standard.

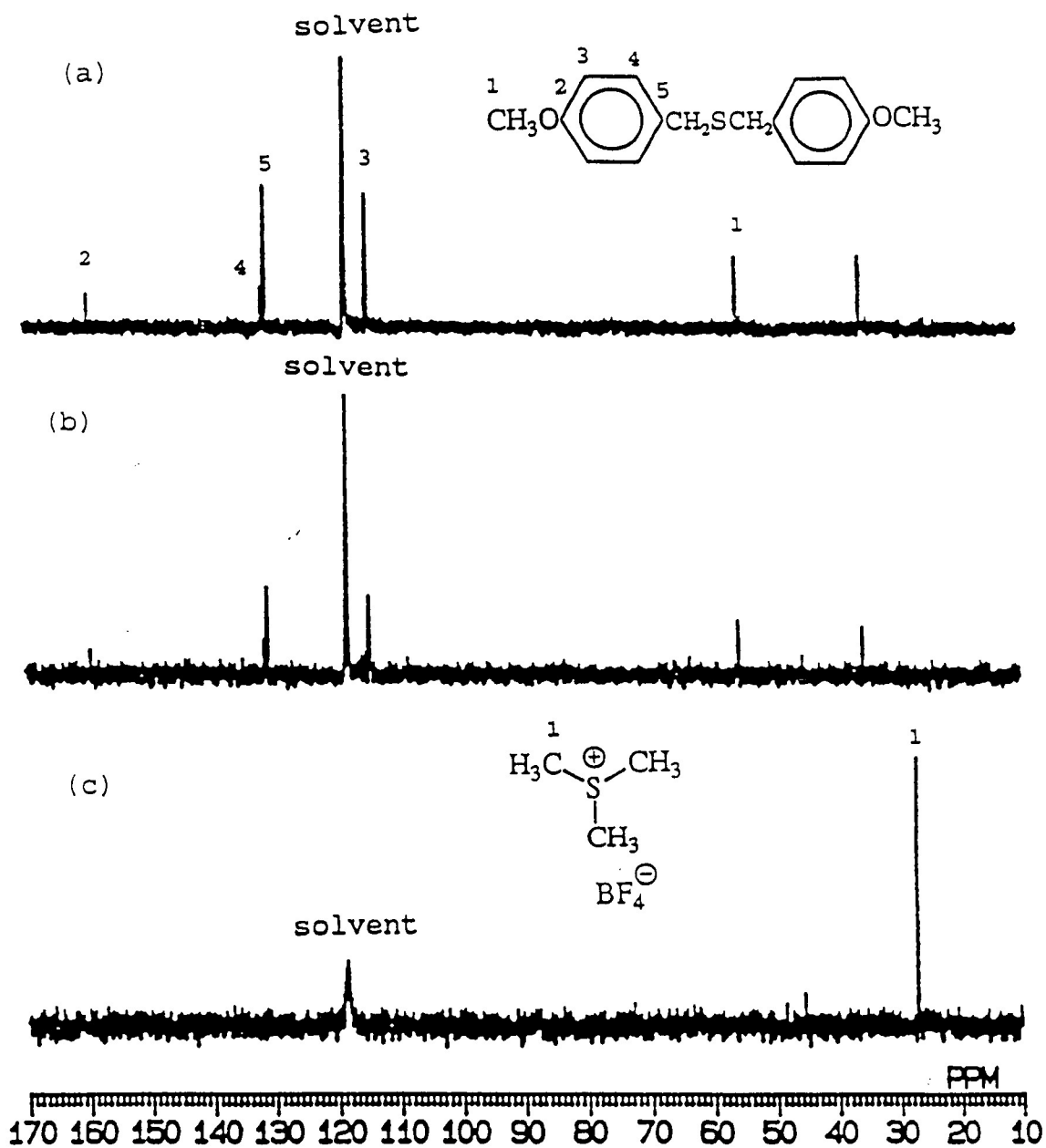


Figure 19. ^{13}C NMR spectra and assignments of $(\text{CH}_3\text{OPhCH}_2)_2\text{S}$ and its methylated products (CD_3CN as solvent, TMS as reference): (a) $(\text{CH}_3\text{OPhCH}_2)_2\text{S}$, (b) $(\text{CH}_3\text{OPhCH}_2)_2\text{S} + \text{CH}_3\text{I}$ without AgBF_4 , CH_3NO_2 as internal standard, and (c) $(\text{CH}_3\text{OPhCH}_2)_2\text{S} + \text{CH}_3\text{I}$ with AgBF_4 , CH_3NO_2 as internal standard.

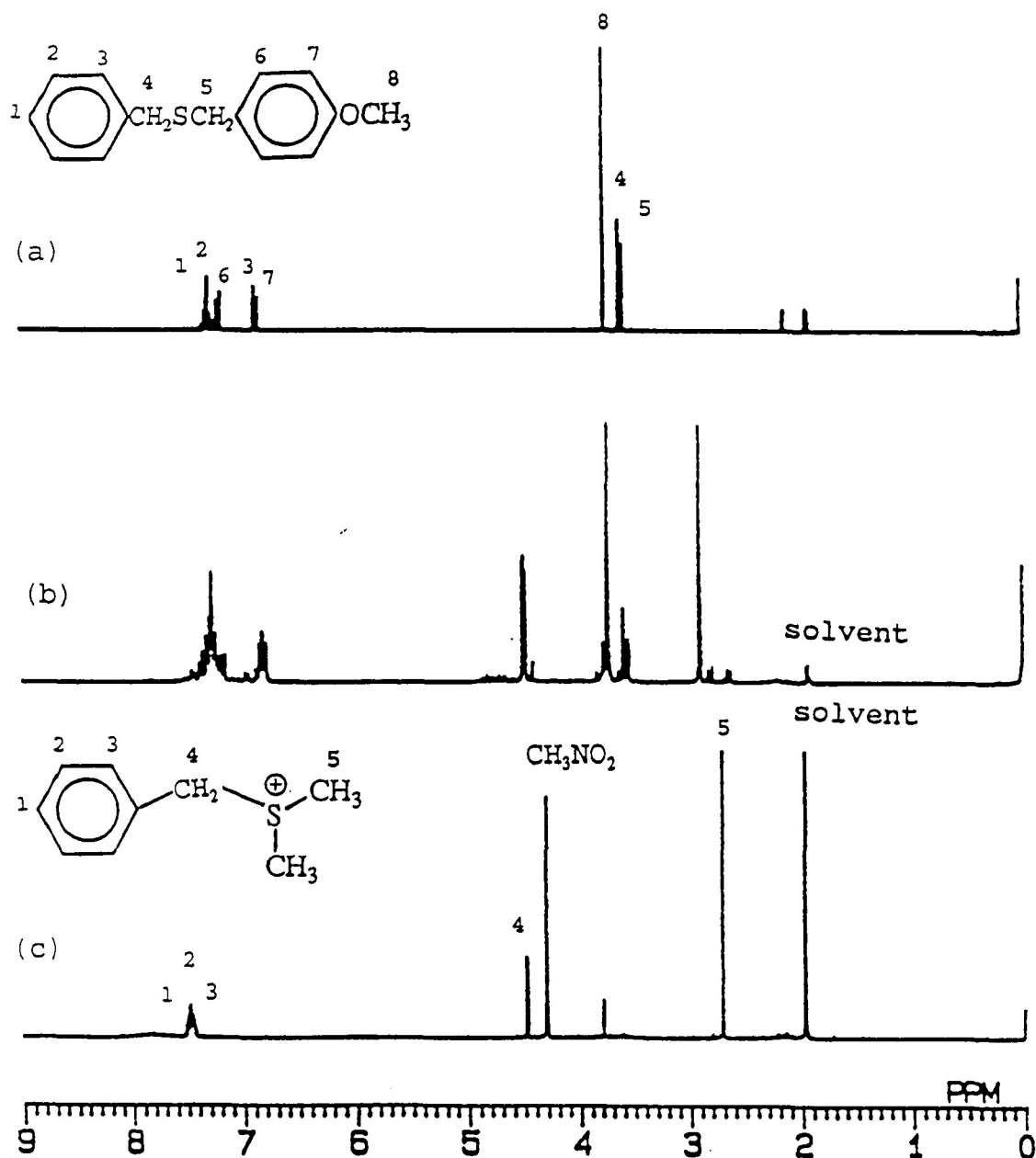


Figure 20. ^1H NMR spectra and assignments of $\text{CH}_3\text{OPhCH}_2\text{SCH}_2\text{Ph}$ and its methylated products (CD_3CN as solvent, TMS as reference): (a) $\text{CH}_3\text{OPhCH}_2\text{SCH}_2\text{Ph}$, (b) $\text{CH}_3\text{OPhCH}_2\text{SCH}_2\text{Ph} + \text{CH}_3\text{I}$ without AgBF_4 , CH_3NO_2 as internal standard, and (c) $\text{CH}_3\text{OPhCH}_2\text{SCH}_2\text{Ph} + \text{CH}_3\text{I}$ with AgBF_4 , CH_3NO_2 as internal standard.

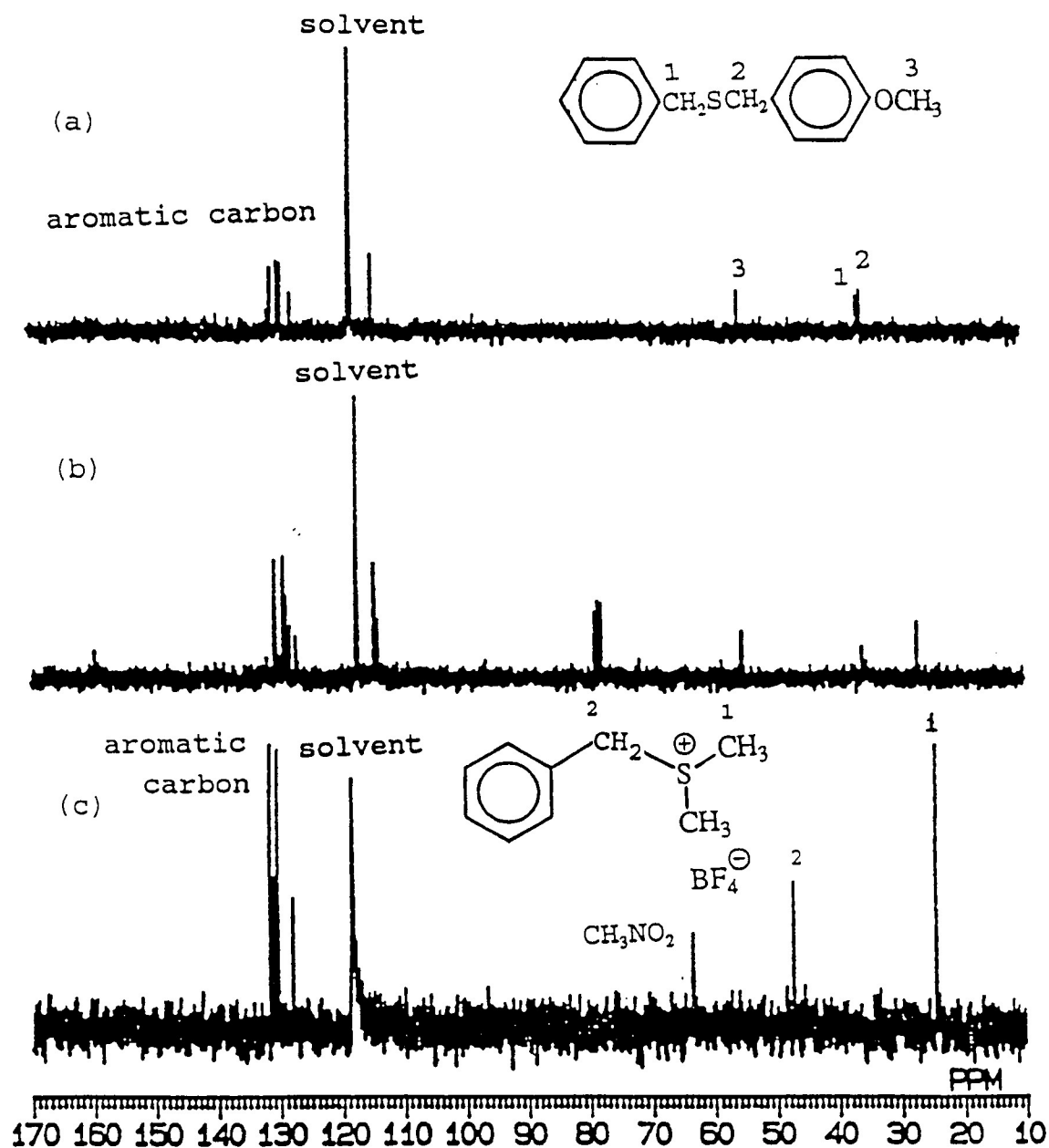


Figure 21. ^{13}C NMR spectra and assignments of $\text{CH}_3\text{OPhCH}_2\text{SCH}_2\text{Ph}$ and its methylated products (CD_3CN as solvent, TMS as reference): (a) $\text{CH}_3\text{OPhCH}_2\text{SCH}_2\text{Ph}$, (b) $\text{CH}_3\text{OPhCH}_2\text{SCH}_2\text{Ph} + \text{CH}_3\text{I}$ without AgBF_4 , CH_3NO_2 as internal standard, and (c) $\text{CH}_3\text{OPhCH}_2\text{SCH}_2\text{Ph} + \text{CH}_3\text{I}$ with AgBF_4 , CH_3NO_2 as internal standard.

The mechanisms for the methylations with the participation of AgBF_4 is illustrated in Figure 22, in which the sulfur-carbon bond cleavage occurred with the participation of electron donating group, methoxy, and the strong nucleophilic ion, BF_4^- .

The percentage yields of methylation can be quantitatively determined by NMR integration techniques using internal standards. The amount of sulfur involved in sulfur-carbon bond cleavage (CH_3NO_2 as internal standard) can be calculated as:

$$\frac{\text{mg of CH}_3\text{NO}_2 * \text{peak area (27ppm)} * 100}{61.04 * \text{peak area (62ppm)} * 89.2 * \text{mmol of original sulfur} * 3} \quad (6)$$

where the factor of 89.2 accounts for isotopic enrichment in the product compared to the internal standard.

We also S-methylated the extract with d_3 -iodomethane and analyzed the product with ^2D NMR. The spectrum is shown in Figure 23, in which the solvent was CH_3CN , and the internal standard was CDCl_3 . The spectrum shows that the peak at 2.8 is methylated sulfide and the peak at 3.2 is methylated thiophenes. The triple peaks observed at 1.9 ppm may result from the transformation of deuterium by chemical exchange between deuterated chloroform or d_3 -iodomethane methylated product and one of the hydrogens in CH_3CN to form CDH_2CN , in which the deuterium peak is split by two hydrogens.

The percentage of total methylated aliphatic and thiophenic sulfur shown in the figure can be calculated as:

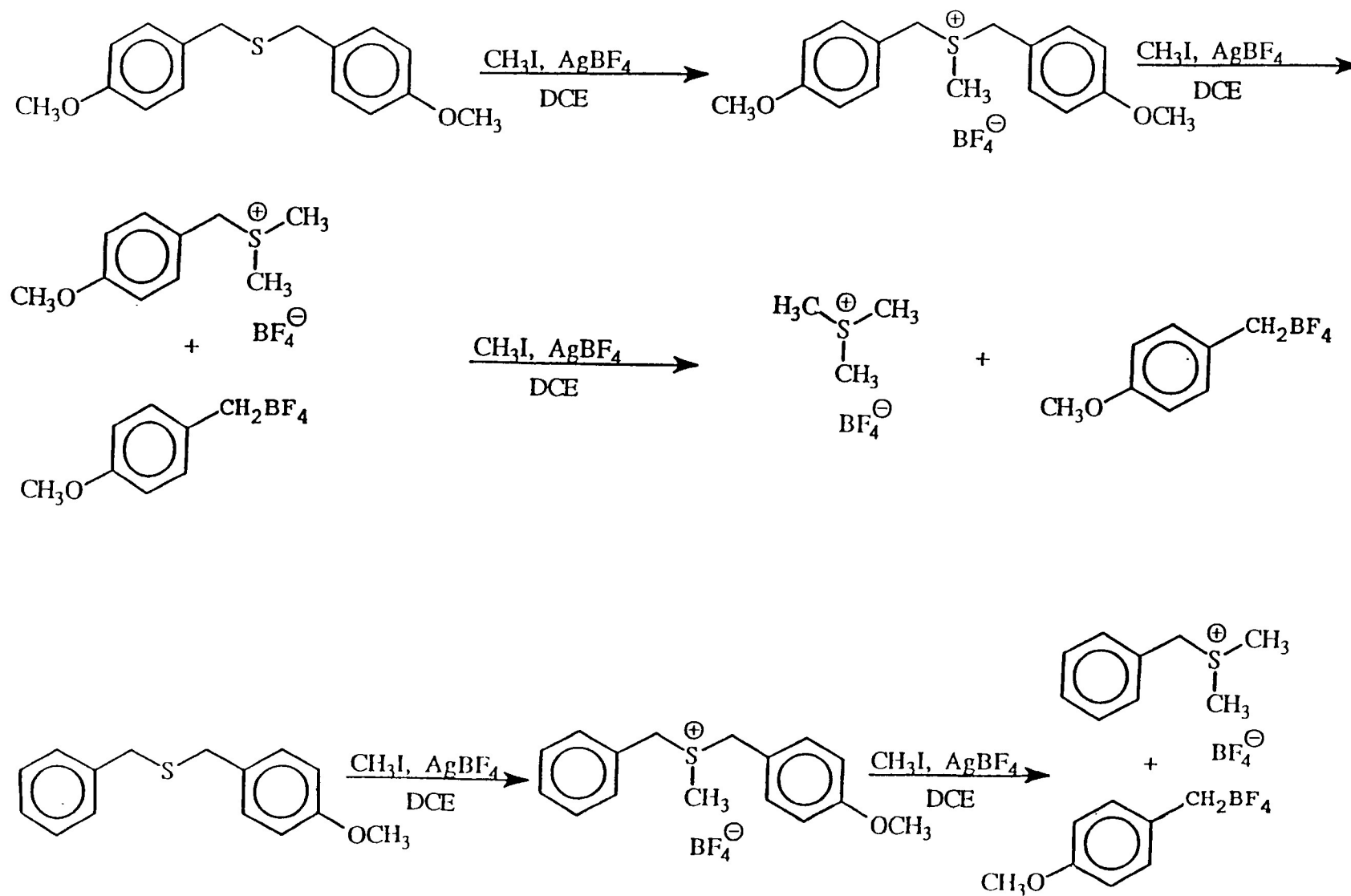


Figure 22. Mechanisms of model sulfide compounds methylation.

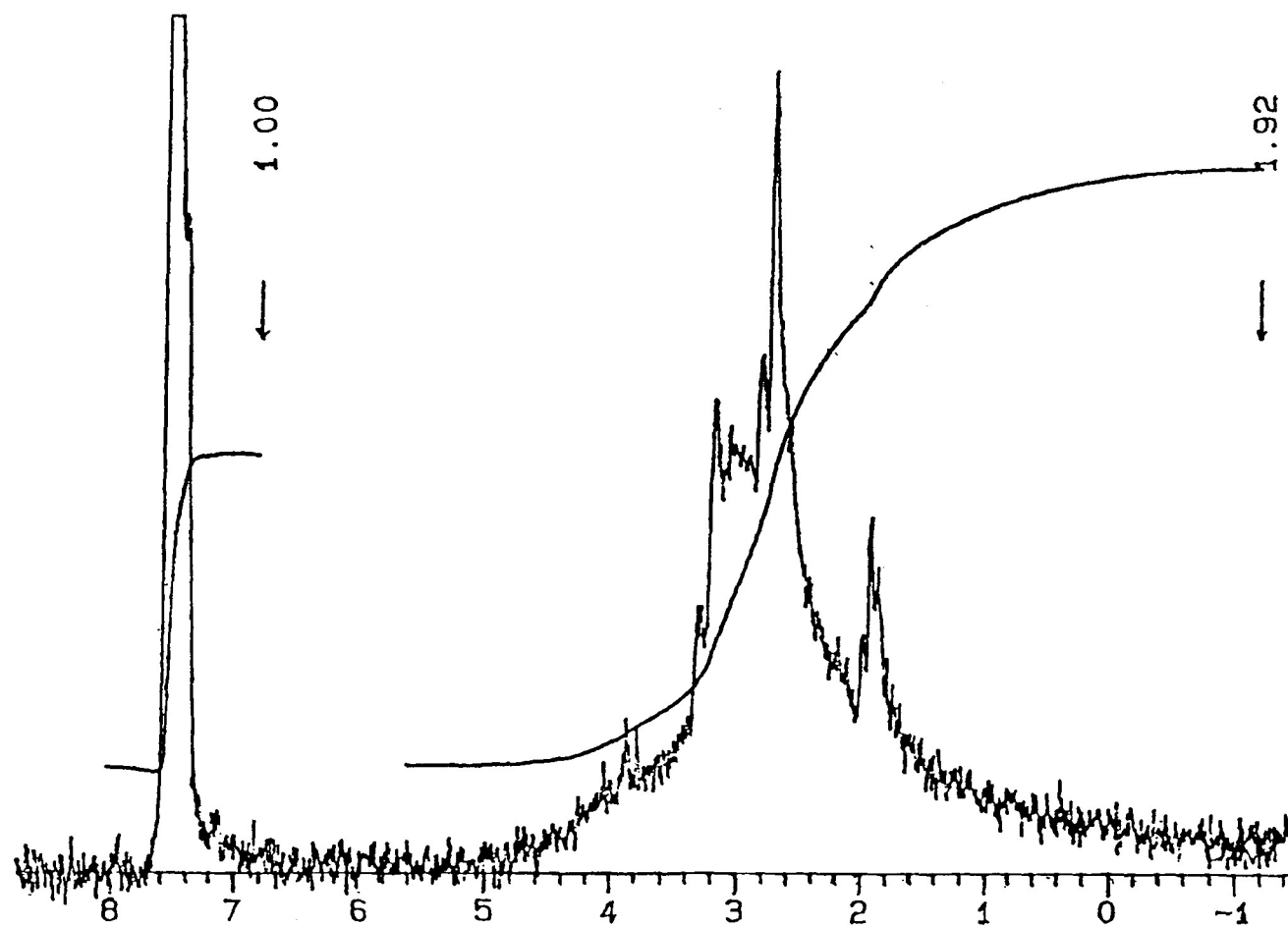


Figure 23. ^2H NMR spectrum of the solid from the coal THF extract methylated by ^{12}C -iodomethane in base, then by d_3 -iodomethane with AgBF_4 (CDCl_3 as internal standard).

$$\frac{\text{mg of CDCl}_3 \cdot \text{peak area (3ppm)} \cdot 100}{120.38 \cdot \text{peak area (7.24ppm)} \cdot \text{mmol of original sulfur} \cdot 3} \quad (7)$$

The total methylated aliphatic and thiophenic sulfur is approximately 20-30% of the total organic sulfur in the coal THF extract.

The results of sulfur methylation on model compounds, coal, and coal extracts are summarized in Table 6. These data indicate that although the percentages of carbon-sulfur bond cleavage in model compounds are 90-100%, the carbon-sulfur cleavage in coal and extracts is lower than expected. It is likely that forms of sulfur species such as $(\text{CH}_3\text{OPhCH}_2)_2\text{S}$, $\text{CH}_3\text{OPhCH}_2\text{SH}$, and $\text{CH}_3\text{OPhCH}_2\text{SCH}_3$ are lower in the coal and extract. Due to the complexity of coal, the optimum conditions for the cleavage of sulfur-carbon bonds needs further investigation.

Table 6. Chemical Shifts and Yields of Sulfur Methylation^A

Starting Substances	δ_C ppm	δ_H ppm	% of Yield
$(CH_3)_2S + CH_3I$	27.44	2.90	74.11 ^B
$(CH_3)_2S + CH_3I / AgBF_4$	27.33	2.84	82.23 ^B
$(CH_3OPhCH_2)_2S$ + $CH_3I / AgBF_4$	27.28	2.81	91.48
$CH_3OPhCH_2SCH_2Ph$ + $CH_3I / AgBF_4$	24.60	2.72	115
Raw coal 90008 + $^{13}CH_3I / AgBF_4$	26.84	-	1.89
Coal 90008 THF extract + $^{13}CH_3I / AgBF_4$	27.22	-	2.17

^A CD_3CN as solvent, CH_3NO_2 as internal standard.

^B Calculation based on weighed product.

Chapter IV

CONCLUSIONS AND FURTHER WORK

Coal extraction is a significant technique for investigating organic species in coal, as well as structure of the parent coal, since the extract and mineral-matter-free coal have similar chemical composition, as determined by ultimate analysis and FTIR instrumentation.

TG-FTIR spectrometry provides detailed information about the controlled oxidation of organic sulfur in coal, in coal extracts, and in coals partially oxidized in air.

Sulfur-carbon bond cleavage in coal during sulfur methylation in the presence of AgBF_4 was confirmed and quantified as approximately 2%. The total sulfur that can be methylated in coal and its extracts is about 20-30%.

Throughout this research, work was performed on one specific coal and specific solvents. For more detailed information about the behavior of organic sulfur in coal, further investigations are suggested:

1. The relationship between coal solvent extraction and the parent coal is not entirely affirmed. Selecting different solvents such as benzene or cyclohexane to be run on a wide range of coals is necessary to unravel the

similarity between coal extracts and their precursor coal structure.

2. Although the sulfur-carbon bond cleavage took place in the presence of AgBF_4 , the cleavage yield was as low as 2%. It is necessary to find the optimum conditions to increase the yield of sulfur-carbon bond cleavage for further quantitative determinations of aliphatic sulfur.

3. As indicated in the ^{13}C NMR spectra of ^{13}C -enriched sulfur methylated raw coal and its THF extract show some thiophenic sulfonium ions were present. The best approach for identifying these species is to make model thiophenic sulfonium compounds to determine whether they match the sulfonium groups from methylating raw coal and extracts. Spiking the methylated raw coal and extracts with these model thiophenic sulfonium compounds will allow the quantitative speciation of the thiophenic sulfur compounds in coal.

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